

Analytic solution for the nonequilibrium
pair-correlation function and
the non-Newtonian viscosity coefficients
of simple liquids

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I. Introduction

In a dense fluid the individual molecules are strongly correlated with each other by the intermolecular forces. For the case where the interaction potential of molecules is pairwise additive, the most important correlation among the individual molecules may be represented by the pair-correlation function $g(\underline{R}_1, \underline{R}_2)$ (in nonequilibrium generally). It is the measure of the probability to find a molecule at $\underline{R}_1$ knowing the presence of another at $\underline{R}_2$ in the pair-particle configurational space of a fluid system. This function is very important in many-body systems (in non-fluid systems the definition of g should be somewhat different from that stated here), for the structure factor (its Fourier transformation) may be observed directly by experiments, e.g. by X-ray or neutron scattering/T-S/, and many of the important thermodynamic properties can be explained by it. The equilibrium pair-correlation function g_0 is determined by the canonical distribution. But in nonequilibrium the pair-correlation function g may be deduced from the mechanical law which describes the movements of the individual molecules microscopically, for which one has the well-known BBGKY hierarchy/KIR1, RIC, BAL/. In 1946 J.G. Kirkwood derived the generalized Fokker-Planck equation starting from the Liouville's equation, which will be introduced in this work as the foremost point of departure.

The viscosity coefficient (here not only the shear viscosity but also the viscosity coefficients of normal-pressure difference) is mainly determined by the (potential) contribution from intermolecular forces in a liquid. The kinetic contribution due to direct momentum transfer is relatively small /KIR2/. For this reason the former only is considered here. This potential contribution to the viscosity coefficient may be calculated by using the nonequilibrium pair-correlation function g /KIR2, RIC/, more exactly by using the deviation from its equilibrium value g_0 . Thus some of the most important

properties of the deviation ($g - g_0$) will be transferred to the viscosity coefficients, e.g. the behavior near the (liquid-gas or fluid-solid) phase transition. Until now the behavior of viscosity coefficients near the phase transitions is not well understood. Many of the recent workers /COH,EHH,EU,EVA,KAW/ are interested also in the functional dependence of viscosity coefficient on the shear rate, which is not yet completely understood, too, even for the limiting case of a small shear rate.

Kirkwood also derived an equation for the pair-distribution function $\rho^{(2)}(\underline{R}_1, \underline{R}_2) = \rho^{(1)} \rho^{(1)} g(\underline{R}_1, \underline{R}_2)$ from his generalized Fokker-Planck equation in order to calculate the potential contribution to the Newtonian viscosity /KIR2/, where $\rho^{(1)}$ is the one-particle distribution function. This was one of his pioneering works. In deriving this equation he assumed tacitly small flow velocity and a small shear rate to avoid the nonlinear terms, and introduced a simple ansatz for the equilibrium pair-correlation function to calculate the perturbation function explicitly. This Kirkwood's equation for $\rho^{(2)}$ is extended here to large flow velocities and shear rate by showing the term nonlinear in flow velocity and the time derivative term of flow velocity explicitly. It is possible that the nonlinear term vanishes identically in some special geometry of flow, which is essentially different from the linearization.

The interesting properties associated with g_0 cannot be preserved by such a simple ansatz like that made by Kirkwood et al. /KIR2/. Its characteristic behavior may be separated in the following two aspects: the behavior near the highest peak of g_0 (or at the repulsive core) and its long-range behavior. The latter is related to the liquid-gas phase transition /BAL,STA/ and the former proves to be associated with the fluid-to-solid-like phase transition found in this work. The Ornstein-Zerike theory /O-Z1/ is introduced and its approximation /O-Z2,ZER,STA/ is here improved to calculate the long-

range behavior of g_0 . In obtaining the explicit condition for the fluid-to-solid-like phase transition it is very important to introduce the effective hard core which represents the repulsive part of the intermolecular potential effectively in a dense fluid, which depends upon both density and temperature. As will be shown in the last chapter, this condition is related to a certain value of the mean force at this effective hard core in the relative pair configurational space.

One of the most important points of this work is the perturbation expansion of the deviation $(g - g_0)$ in the deformation parameter (not the total shear rate) which is the symmetric part of the shear rate tensor. S. Hess stressed always in his lectures and works /HES1,2/ that the shear rate tensor should be separated into its symmetric and its antisymmetric part. It was much later that the idea "perturbation expansion of the deviation $(g - g_0)$ with respect to the deformation parameter" had arisen in the present author's mind. Owing to this perturbation expansion it is possible to obtain a wide variety of functional dependences of the deviation $(g - g_0)$ and the viscosity coefficients on the shear rate, where the rotational parameter (the antisymmetric part of the shear rate tensor) is taken into account correctly as a member of the unperturbed part of the differential operator in the extended Kirkwood-Smoluchowski (K-S) equation for g , which may be derived from the extended K-S-eq. for $\rho^{(2)}$, (2.1.13). In this situation, the viscosity coefficient is not a simple function of the shear rate (by "simple" it is meant here that there are no other parameters except for the scaling factor to change the functional form of the viscosity coefficient), but it is now associated with some important parameters of the equilibrium pair-correlation function, e.g. the correlation length, in an explicit manner.

1.1) Purpose and results

As mentioned above, Kirkwood et al. /KIR2/ established an equation for nonequilibrium pair-distribution function $\rho^{(2)}$. Their purpose was to obtain a quantitative information about the Newtonian viscosity of liquids, where the potential contribution is preponderant over the kinetic one. In order to have some explicit solution they also set up a simple functional form of the equilibrium correlation function $g_0(r)$. Subsequently another workers /ZWA,LOW/ tried to solve the same equation for $g(r)$ in the linear order of shear rate, where they used for g_0 an approximated solution of the integral equations (the Kirkwood equation and the Born-Green-Yvon equation) for g_0 /KIR3/. Since their main interest is to obtain the correct value of the Newtonian viscosity coefficient and their solutions are in the linear order of shear rate, it is difficult to find some qualitative features associated with the properties of g_0 (e.g. its behaviors related to the shear rate near the phase transitions) in their results. Moreover one has to solve a formidable integral equation, which should be solved practically by the machine calculation. But, above all, the critical failure of the theories mentioned above and the like is the following:

At the fluid-to-solid-like phase transition the traditional perturbation expansion in the shear rate diverges no matter how small the shear rate is. At the liquid-gas phase transition it also diverges in the range of scaled shear rate larger than the inverse correlation length (Since the inverse correlation length is practically zero at the liquid-gas phase transition, the expansion of g in shear rate diverges in "almost" whole range of shear rate at this phase transition). They will be discussed in section 3.4) and in chapter IV.

The purpose of this work is to obtain the essential functional dependences of the nonequilibrium pair-correlation function $g(r)$ and the viscosity coefficients on the shear rate, and to see the effects of the particular behaviors of equilibrium

pair-correlation function $g_0(r)$ on them. Here the liquid-gas and the fluid-solid phase transition are meant by the particular behaviors. The results are the following:

- (1) The Kirkwood-Smoluchowski(K-S) equation for the pair-distribution function $\rho^{(2)}(\underline{R}_1, \underline{R}_2; t)$, which is derived from the generalized Fokker-Planck(F-P) equation for the pair-distribution function $f^{(2)}(\underline{R}_1, \underline{R}_2, \underline{v}_1, \underline{v}_2; t)$ by Kirkwood et al., is extended to include the term nonlinear in flow velocity, $\underline{u} \cdot \underline{\nabla} \underline{u}$, and the time derivative term, $\partial \underline{u} / \partial t$, which together constitute an inertial term: $\dot{\underline{u}}_i := \partial \underline{u}_i / \partial t + \underline{u}_i \cdot \underline{\nabla} \underline{u}_i$. In the extended K-S equation obtained here the inertial force $m \dot{\underline{u}}$ is subtracted from the mean force $\underline{F}_i$ due to intermolecular forces and the molecule at $\underline{R}_i$ sees the effective force $\underline{F}_i - \dot{\underline{u}}_i$, as it should be so. The nonlinear term may vanish identically in some geometry of flow, e.g. Couette-flow, which is different from the linearization made by the earlier workers /KIR2, RIC/.
- (2) As was hoped, the wide variety of functional dependences of $g(r)$ and the viscosity coefficients is obtained in explicit functional forms. Their limiting behaviors are examined.
- (3) Both of them show nonanalytic behavior at(or near) the liquid-gas phase transition in quite a wide range of shear rate. This nonanalytic behavior(in the appearance of square-root-shear-rate term) is similar to that suggested by some recent computer experiments/EVA,EHH/. But it is essentially different from the prediction of Kawasaki/KAW/. For example in the present theory the nonanalytic behavior is hardly observed away from the liquid-gas phase transition. The most important implication of this behavior is that at liquid-gas phase transition the perturbation expansion in shear rate fails to converge in the range of scaled(by relaxation time τ) shear rate larger than inverse correlation length, which is practically zero, even if not absolutely zero, at the phase transition.
- (4) The most important result of this work is the discovery of the equation of condition for the fluid-to-solid-like phase

transition. At this phase transition the normal-pressure difference jumps as soon as the shear strain is "switched on". At this phase transition also, the nonanalytic behavior appears in the viscosity coefficients and the perturbation expansion in shear rate does not converge at all. Just near this fluid-to-solid-like phase transition the shear viscosity coefficient has an enormously high and very narrow peak (its half-width is proportional inversely to its height) about the zero shear rate. By using the Wertheim-Thiele solution of the Percus-Yevick equation for hard spheres/WER,THI/ the density at the fluid-to-solid-like phase transition for hard spheres is calculated as $x^* = (1.05)^{1/2} - 0.5 = 0.52 \dots$, which doesn't depart so away from the experimental value $x_{tr} = 0.48$ /A-W/. The deviation from experiments may be caused by the incorrectness of the Percus-Yevick equation itself.

- (5) The Ornstein-Zernike(O-Z) approximation for the density correlation function is corrected and improved. This improved O-Z approximation is necessary to see the solution for $g(r)$ in its complete explicit form and its behavior associated with the liquid-gas phase transition.

Each section is summarized in the following.

1.2) Outline and notations

In section 2.1) the K-S-equation, which may be derived from the generalized F-P-equation due to J.G.Kirkwood/KIR/, is extended to the large values of flow velocities and shear rates. This extended K-S-equation obtained here differs in form from that derived by the earlier workers in containing the time derivative and the nonlinear term, $\partial \underline{u} / \partial t + \underline{u} \cdot \nabla \underline{u}$. As mentioned above, these terms vanish identically in some special geometry of stationary flows and the extended K-S-equation becomes similar to the old K-S-equation in the stationary case. But the latter cannot be applied to a wide range of shear rate in its own reasoning, while the former can. The approximations in deriving the extended K-S-equation are discussed.

In section 2.2) the most important start for the later parts of this work is made: The deviation of $g(r)$ from equilibrium is expanded in the deformation parameter (the symmetric part of shear-rate tensor) and the rotational part of the flow term in the K-S equation is included exactly in the unperturbed differential operator. Here the liquid system is assumed to be in stationary state as an approximation (the effect of dilatation in shear flow/ZWA/ is here neglected). The K-S equation is transformed for the unperturbed differential operator to be hermitian with the corresponding boundary conditions. A system of partial differential equations for the perturbation functions is obtained and it is enormously reduced by using the hermitian property of the differential operator.

In section 3.1) an useful ansatz for the intermolecular potential is introduced. It consists of a long-range attractive part and a hard core which may represent the repulsive part of some realistic potential effectively. The hard core provides us with a convenient boundary condition. The potential ansatz (3.1.1) introduced here is based on the work of J.D. Weeks, D. Chandler, and H.C. Andersen/AND, WEE/. They showed that the equilibrium pair-correlation function of the dense Lennard-



Jones(L-J) fluid may be replaced by $\exp(-v_{LJ}^{(r)}/k_B T) y_\sigma$ as a good approximation, where $v_{LJ}^{(r)}$ is the repulsive part of L-J potential and $y_\sigma = \exp(v_\sigma/k_B T) g_\sigma$ (v_σ is the hard-sphere potential with the effective diameter σ ; g_σ is the pair-correlation function of hard spheres with diameter σ). In this work this approximation is not used but the potential type (3.1.1) is simply introduced as an ansatz, even if the effective diameter may be determined by the rule stated in/AND, WEE/. When the hard-core part of the potential (3.1.1) represents the repulsive part of the realistic potential effectively, the error in the excess (potential contribution) Helmholtz free energy is estimated.

In section 3.2) the Ornstein-Zernike theory is introduced to obtain the functional form of equilibrium pair-correlation function g_0 . It is found that some correction is inevitable in the approximation process made by them and the subsequent workers. The usual approximation is extensively improved. The equilibrium pair-correlation function g_0 for hard spheres is calculated explicitly by using the Wertheim-Thiele solution of the Percus-Yevick equation for hard spheres. It is avoided here to solve directly the more explicit but approximated integral equations for g_0 (like the Kirkwood-, the BGY-, and the P-Y-equation), for the main interest in this work is to see the relations of g_0 to the thermodynamic variables in an explicit manner. This explicit functional form of g_0 is used later to calculate the perturbation functions explicitly.

In section 3.3) the general solution for the deviation factor is obtained in the first-order approximation in the deformation parameter. Another approximation is made in employing the zeroth-order Green's function (with respect to the perturbation $V_0(r)$ defined in (3.3.5)'). But in this approximation the effect of the long-range behavior of g_0 on the deviation factor is preserved. The Green's function may be improved systematically by (3.3.7)'. To see the deviation factor explicitly the improved O-Z approximation for g_0 is substituted in the general

solution.

In section 3.4) the limiting behaviors of deviation factor are examined in the relation to the liquid-gas phase transition especially. At(or near) this transition the deviation factor behaves nonanalytically in the range of scaled(by relaxation time τ) shear rate larger than the inverse correlation length. This implies the divergence of the traditional perturbation expansion with respect to the (total) shear rate in this range of shear rate. The limiting features at (or near) the fluid-to-solid-like phase transition are not examined in this section, but some important points are discussed in remarks.

In section 4.1) the general solutions for the non-Newtonian viscosity coefficients are obtained. They are also calculated in their complete explicit forms for hard spheres by using the improved O-Z approximation for g_0 developed in section 3.2).

In section 4.2) the limiting behaviors of viscosity coefficients associated with the liquid-gas phase transition are examined in a similar manner to that of section 3.4). The viscosity coefficients also show the nonanalytic behavior in the range of scaled shear rate larger than the inverse correlation length. The numerical calculation is not executed for the lack of knowledge about g_0 . Since the hard-sphere system doesn't undergo the liquid-gas phase transition, the hard-sphere pair-correlation function cannot be applied to examine this non-analytic behavior.

In section 4.3) an exotic behavior of normal pressure difference is found under a certain condition, which is here considered as the fluid-to-solid-like phase transition. An interesting equation for this behavior is obtained and tested by using the W-T solution of the P-Y equation for hard spheres, as mentioned above. Some interesting behaviors of viscosity coefficients are examined just near this phase transition.

In section 4.4) the viscosity coefficients of hard spheres are displayed graphically, where the W-T solution of the P-Y equation for hard spheres is used. Some remarks for these pictures are added.

Notations

/.../ references

(...) comments

$a^+ := \lim_{0 < \epsilon \rightarrow 0} (a + \epsilon)$

Re real part of

σ diameter of a hard sphere (or hard core of the inter-molecular potential introduced in the section 3.1))

D diffusion constant

$\tau := \sigma^2/D$ (relaxation time coefficient)

T_* $:= k_B T$

k_B Boltzmann constant

ζ friction constant

$\underline{R}$ coordinate vector

$\underline{r} := \underline{R}/\sigma$ dimensionless coordinate vector

$\nabla_x := \partial/\partial x$

$\nabla := \partial/\partial \underline{r}$

$\nabla^2 := \nabla \cdot \nabla$

γ	shear rate
γ_r	rotational parameter of the shear rate tensor
γ_d	deformation parameter of the shear rate tensor
$(\eta_+)P_+$	(viscosity coefficient of) shear pressure
$(\eta_-)P_-$	(viscosity coefficient of) normal-pressure difference between x- and y-direction
$(\eta_0)P_0$	(viscosity coefficient of) the difference of normal pressure in z-direction from the average of those in x- and y-direction
$(g)g_0$	(non-)equilibrium pair-correlation function
$\tilde{g}_0$	$:= g_0(1^+)$ for $r=1$, and $g_0(r)$ for $r>1$
$w(r)$	$= -k_B T \ln g_0$ potential of mean force in relative pair space
w_1	$:= (2T_*)^{-1} (dw(r)/dr)_{r=1^+}$
Δw_1	$:= 3 - w_1$
g_σ	equilibrium pair-correlation function for hard spheres with diameter σ
$s(r)$	$:= g_0(r) - 1$ density-density correlation function in equilibrium
$s_1^>$	$:= s(1^+)$
ψ, χ	deviation factors defined by $g = g_0(1+\chi) = g_0(1+g_0^{-1/2}\psi)$

II. Hierarchy of equations for the deviation of pair-correlation function from equilibrium

The basis of this work is the generalized Fokker-Planck(F-P) equation for the pair-distribution function which depends upon both positions and velocities in pair-particle space. This equation is derived by J.G. Kirkwood/KIR1/ starting from the Liouville equation. In his theory the friction coefficient is related to the intermolecular potential in an explicit manner, which is the crucial difference from the Chandrasekhar's generalized F-P equation/CHA/. The Chandrasekhar's starting point is the Langevin equation with the stochastic force term and the friction coefficient as an empirical constant. A few years later J.G. Kirkwood and his coworkers derived from the generalized F-P equation an equation for the pair-distribution function depending upon the positions only in pair space to calculate the potential contribution to the viscosity coefficient by introducing a simple ansatz for the equilibrium pair-correlation function/KIR2/. This equation for the configurational pair-distribution function is a projection of the generalized F-P equation for the pair-distribution function dependent upon both positions and velocities in pair space onto 6-dimensional configuration space, and similar to the Smoluchowski equation for one particle distribution function in configuration space/RIC/. Thus in this work this equation is named as the Kirkwood- Smoluchowski(K-S) equation/HES1/.

But the extended K-S equation to be derived in this work is somewhat different from that of Kirkwood/KIR2/ in the appearance of the term nonlinear in flow velocity, which is neglected in the Kirkwood's equation under the linearization process from the beginning of derivation/KIR2,RIC/, and in that of the time derivative term of flow velocity. Therefore the Kirkwood's equation is restricted to a small shear-rate range in its own reasoning. It is very important to preserve the term nonlinear in flow velocity correctly and let it be zero not through the linearization but through the very property of flow, so that

the equation may be also applicable to quite a large shear-rate region. In the Couette-flow geometry the term nonlinear in the flow velocity vanishes identically and the K-S equation extended in this work is valid also in a moderately large shear-rate region. This extended K-S equation is the starting point for the main part of this work.

The friction coefficient will be treated in this work as a phenomenological parameter. This can be determined by comparing the calculated shear viscosity coefficient at the zero shear rate with the experimental data of Newtonian viscosity coefficient.

2.1) Extension of the Kirkwood-Smoluchowski equation for the configurational pair-distribution function and remarks

The F-P equation for the pair-distribution function which depends upon both position and velocity is given by/KIR2/:

$$\begin{aligned} \partial f^{(2)} / \partial t + \underline{v}_1 \cdot \nabla_{R1} f^{(2)} + \underline{v}_2 \cdot \nabla_{R2} f^{(2)} + m^{-1} \nabla_{v1} \cdot (\underline{F}_1 f^{(2)}) + \\ + m^{-1} \nabla_{v2} \cdot (\underline{F}_2 f^{(2)}) = \quad (\zeta/m) \nabla_{v1} \cdot \{ \underline{v}_1 f^{(2)} + (k_B T/m) \nabla_{v1} f^{(2)} \} \\ + (\zeta/m) \nabla_{v2} \cdot \{ \underline{v}_2 f^{(2)} + (k_B T/m) \nabla_{v2} f^{(2)} \}. \end{aligned} \quad (2.1.1)$$

The quantities in the above equation are defined as follows.

$\rho^{(1)}(\underline{R}_i) := (N-1)^{-1} \int f^{(2)} d\underline{v}_1 d\underline{v}_2 d\underline{R}_j \quad (i+j=1,2)$: number density at $\underline{R}_i$

$\underline{u}_i := \underline{u}_i(\underline{R}_i) := \{ (N-1) \rho^{(1)}(\underline{R}_i) \}^{-1} \int \underline{v}_i f^{(2)} d\underline{v}_1 d\underline{v}_2 d\underline{R}_j \quad (i+j=1,2)$
: flow velocity at $\underline{R}_i$

$\underline{v}_i := \underline{v}_i - \underline{u}_i$ peculiar velocity of a molecule at $\underline{R}_i$

$\underline{F}_i$: mean force acting on a molecule at $\underline{R}_i$ in the presence of another at $\underline{R}_j$ ($i+j=1,2$) in nonequilibrium generally

ζ : friction coefficient (here assumed to be uniform and isotropic)

k_B : Boltzmann constant

T : temperature

N : total number of molecules

m : molecular mass (2.1.1A)

In projecting the equation (2.1.1) onto the 6-dimensional configuration space it is more natural to take into account the moments of the peculiar velocities $\underline{v}_i$ defined by (2.1.1A) than those of the actual velocities $\underline{v}_i / HES1/$. On multiplying eq. (2.1.1) by the following quantities

$$1 \text{ or } \underline{v}_{i1} \cdots \underline{v}_{in} \quad (i1, \dots, in = 1, 2 \text{ and } n = 1, 2, 3 \dots)$$

and integrating over $\underline{v}_1$ and $\underline{v}_2$, one obtains a system of equations of change for

$$\rho^{(2)} \text{ and } J_{i;1\dots n} := \int \underline{v}_{i1} \cdots \underline{v}_{in} f^{(2)} d\underline{v}_1 d\underline{v}_2 \quad (n=1, 2, 3, \dots).$$

These are the moment equations in $(\underline{R}_1, \underline{R}_2)$ space and they are coupled with each other. Some pertinent approximations should be introduced to obtain a closed equation for the quantity of interest. Here the closed equation for the pair-distribution function $\rho^{(2)}(\underline{R}_1, \underline{R}_2)$ defined by

$$\rho^{(2)} := \int f^{(2)} d\underline{v}_1 d\underline{v}_2 \quad (2.1.2)$$

is desired, with which one can calculate the potential contribution to the viscosity coefficients. Integration of eq. (2.1.1) over $\underline{v}_1$ and $\underline{v}_2$ leads to the equation of continuity for $\rho^{(2)}(\underline{R}_1, \underline{R}_2)$, i.e.

$$\partial \rho^{(2)} / \partial t + \nabla_{\underline{R}_1} \cdot (\underline{u}_1 \rho^{(2)}) + \nabla_{\underline{R}_2} \cdot (\underline{u}_2 \rho^{(2)}) + \nabla_{\underline{R}_1} \cdot \underline{J}_1^{(2)} + \nabla_{\underline{R}_2} \cdot \underline{J}_2^{(2)} = 0$$

$$\underline{J}_i^{(2)} := \int \underline{v}_i f^{(2)} d\underline{v}_1 d\underline{v}_2 = \int (\underline{v}_i - \underline{u}_i) f^{(2)} d\underline{v}_1 d\underline{v}_2, \quad (2.1.3)$$

where $\underline{J}_i^{(2)}$ is the excess probability current density at $\underline{R}_i$ in the presence of a molecule at $\underline{R}_j$ ($i \neq j=1, 2$) in the $(\underline{R}_1, \underline{R}_2)$ space, and

$$\underline{J}_i^{(2)} = \int \underline{v}_i f^{(2)} d\underline{v}_1 d\underline{v}_2 - \underline{u}_i \rho^{(2)} \neq 0 \text{ in general.}$$

The terms disappeared in obtaining (2.1.3) are due to the

following boundary condition for $f^{(2)}$:

$$f^{(2)} \rightarrow 0 \quad \text{as} \quad |\underline{v}_i| \rightarrow \infty \quad (i=1,2).$$

On multiplying eq. (2.1.1) by $\underline{v}_i$ and integrating over $\underline{v}_1$ and $\underline{v}_2$ one obtains the equation for $\underline{J}_i^{(2)}$ as follows

$$\begin{aligned} \partial \underline{J}_i^{(2)} / \partial t + \nabla_{R1} \cdot (\underline{u}_1 \underline{J}_i^{(2)}) + \nabla_{R2} \cdot (\underline{u}_2 \underline{J}_i^{(2)}) + \underline{J}_i^{(2)} \cdot \nabla_{Ri} \underline{u}_i \\ + \rho^{(2)} (\partial \underline{u}_i / \partial t + \underline{u}_i \cdot \nabla_{Ri} \underline{u}_i - \underline{F}_i / m) + \nabla_{R1} \cdot \int \underline{v}_1 \underline{v}_i f^{(2)} d\underline{v}_1 d\underline{v}_2 \\ + \nabla_{R2} \cdot \int \underline{v}_2 \underline{v}_i f^{(2)} d\underline{v}_1 d\underline{v}_2 = -(\zeta/m) \underline{J}_i^{(2)}, \end{aligned} \quad (2.1.4)$$

where again, as in eq. (2.1.3), the boundary condition for $f^{(2)}$ is used for the vanishing integrals. Since the excess probability current density

$$\underline{J}_i^{(2)} =: \underline{\bar{v}}_i^{(2)} \rho^{(2)}(\underline{R}_1, \underline{R}_2) \quad (2.1.5)$$

($\underline{\bar{v}}_i^{(2)}$): peculiar mean velocity at $\underline{R}_i$ in the presence of a molecule at $\underline{R}_j$ ($i \neq j=1,2$) in the $(\underline{R}_1, \underline{R}_2)$ space)

is small, the velocity-velocity correlation of the pair molecules at $\underline{R}_1$ and $\underline{R}_2$ and the nondiagonal component-component correlation of velocity of a molecule at $\underline{R}_i$,

$$\begin{aligned} |\int \underline{v}_1 \underline{v}_2 f^{(2)} d\underline{v}_1 d\underline{v}_2| &\leq |\underline{\bar{v}}_1^{(2)} \underline{\bar{v}}_2^{(2)} \rho^{(2)}| = |\underline{J}_1^{(2)} \underline{J}_2^{(2)}| / \rho^{(2)} \quad \text{and} \\ |\int \underline{v}_{i\mu} \underline{v}_{iv} f^{(2)} d\underline{v}_1 d\underline{v}_2| &\leq |\underline{\bar{v}}_{i\mu}^{(2)} \underline{\bar{v}}_{iv}^{(2)} \rho^{(2)}| = |\underline{J}_{i\mu}^{(2)} \underline{J}_{iv}^{(2)}| / \rho^{(2)} \\ (i=1,2; \mu \neq v = 1,2,3 : \text{Cartesian components}) \end{aligned} \quad (2.1.6)$$

respectively,

are still smaller and may be neglected for the first order approximation in $\underline{J}_i^{(2)}$. But the diagonal component-component correlation of velocity of a molecule at $\underline{R}_i$ is related to the

definition of the temperature by

$$\begin{aligned} \int \underline{v}_i \cdot \underline{v}_i f^{(2)} d\underline{v}_1 d\underline{v}_2 &= (3/m) k_B T_i^{(2)} \rho^{(2)} \\ k_B T_i &:= ((N-1) \rho^{(1)}(\underline{R}_i))^{-1} \int k_B T_i^{(2)} \rho^{(2)} d\underline{R}_j \\ &= (m/3) / \rho^{(1)}(\underline{R}_i) \int \underline{v}_i \cdot \underline{v}_i f^{(1)} d\underline{v}_i \end{aligned}$$

T_i : temperature at $\underline{R}_i$

N : total number of molecules

$$i \neq j = 1, 2, \quad (2.1.7)$$

and should be preserved.

If it is assumed in eq.(2.1.7) that the dependence of $T_i^{(2)}$ on $\underline{R}_j$ ($i \neq j$) is small, $T_i^{(2)}$ ($i = 1, 2$) can be approximated by the corresponding temperature:

$$T_i^{(2)} = T_i \quad \text{for } i = 1, 2. \quad (2.1.8)$$

One can also write

$$\int (\underline{v}_i \underline{v}_i - 1/3 \underline{\delta} \underline{v}_i \cdot \underline{v}_i) f^{(2)} d\underline{v}_1 d\underline{v}_2 \approx 0 \quad (2.1.9)$$

$\underline{\delta}$: 3x3 identity matrix,

for differences among diagonal components of the kinetic pressure tensor may be neglected comparing with the absolute value of the isotropic kinetic pressure. Substitution of eq.(2.1.7) with the approximation (2.1.8-9) into eq.(2.1.4) and neglecting of the terms nonlinear in $\underline{J}_i$ with the arguments (2.1.6) lead to

$$\begin{aligned} \underline{J}_i^{(2)} &= (1/\zeta) \left(-k_B \nabla_{Ri} (T_i \rho^{(2)}) - m \rho^{(2)} (\partial \underline{u}_i / \partial t + \underline{u}_i \cdot \nabla_{Ri} \underline{u}_i - \underline{F}_i / m) \right) \\ &\quad + O_i \\ O_i &:= -(m/\zeta) \left(\partial \underline{J}_i^{(2)} / \partial t + \nabla_{R1} \cdot (\underline{u}_1 \underline{J}_i^{(2)}) + \nabla_{R2} \cdot (\underline{u}_2 \underline{J}_i^{(2)}) + \underline{J}_i^{(2)} \cdot \nabla_{Ri} \underline{u}_i \right). \end{aligned} \quad (2.1.10)$$

For the first order approximation in $(1/\zeta)$ one can neglect the second term and obtains

$$\underline{J}_i^{(2)} \approx (1/\zeta) \left(-k_B \nabla_{Ri} (T_i \rho^{(2)}) - m \rho^{(2)} (\partial \underline{u}_i / \partial t + \underline{u}_i \cdot \nabla_{Ri} \underline{u}_i - \underline{F}_i / m) \right), \quad (2.1.11)$$

where the approximation has been made formally and its validity will be explained in the following.

As usually made, here the first order approximation (2.1.11) is introduced. But it is not clear yet to what extent this first order approximation (2.1.11) may be used, and this should be clarified, not formally, but in terms of some comparable quantities (at least qualitatively).

We will now show under some considerations that the contribution of O_i to the equation (2.1.3) is negligible comparing with $\underline{J}_i^{(2)}$. The second term of eq.(2.1.10) neglected in the first order approximation may be rewritten as

$$\begin{aligned} O_i &= - (m/\zeta) \left(\partial \underline{J}_i^{(2)} / \partial t + \sum_{j=1}^2 \underline{u}_j \cdot \nabla_{Rj} \underline{J}_i^{(2)} \right) \\ &\quad - (m/\zeta) \sum_{j=1}^2 \underline{J}_i^{(2)} d/dt \{ 1/\rho^{(1)}(\underline{R}_j) \} \\ &\quad - (m/\zeta) \underline{J}_i^{(2)} \cdot \nabla_{Ri} \underline{u}_i, \end{aligned} \quad (2.1.12A)$$

where the equation of continuity for the one-particle distribu-

tion function $\rho^{(1)}(\underline{R}_j)$,

$$\partial/\partial t \rho^{(1)}(\underline{R}_j) + \nabla_{\underline{R}_j} \cdot \{\underline{u}_j \rho^{(1)}(\underline{R}_j)\} = 0 \text{ for } j=1,2, \quad (2.1.12B)$$

has been used, and $d/dt := \partial/\partial t + \underline{u}_j \cdot \nabla_{\underline{R}_j}$ for $j=1,2$.

The first term of Eq.(2.1.12A) is related to the time variation of $\underline{J}_i^{(2)}$ in the 6-dimensional configuration space moving with the flow velocity $(\underline{u}_1, \underline{u}_2)$ with respect to the reference space $(\underline{R}_1, \underline{R}_2)$. The second term is proportional to the variation of $\rho^{(1)}$ for the observer moving with the flow velocity $\underline{u}_j$ ($j=1,2$) in 3-dimensional configuration space. Thus the sum of the first and the second term of Eq.(2.1.12A) is roughly proportional to

$$m/(\zeta t_r) \cdot (\text{some quantity in the order of } \underline{J}_i^{(2)}), \quad (2.1.12C)$$

where t_r is the relaxation time in which a significant change in the configurational pair-distrib. function $\rho^{(2)}$ (not $f^{(2)}$!) occurs. The friction constant divided by m , ζ/m , is approximately the number of collisions of a molecule with surrounding molecules per unit time. If one makes use of the "Stoßzahlansatz" /EHR/, one obtains for ζ/m

$$\zeta/m \approx 1/t_{mfp}$$

$$\approx (\text{effective cross section of a molecule}) \cdot (\text{mean speed})$$

$$\cdot (\text{number density})$$

$$= (\pi \sigma^2) \cdot (8k_B T / (\pi m))^{1/2} \cdot (n_0), \quad (2.1.12D)$$

where t_{mfp} and σ are the mean free path time and the effective diameter of a molecule respectively, and the mean speed is not equal to the mean square root speed ($s. /REI/$).

Under the above considerations, (2.1.12C,D), the expression

for small terms Eq.(2.1.12A) may be written as follows

$$O_i = (t_{mfp}/t_r) (\text{some quantity in the order of } \underline{J}_i^{(2)}) - (m/\zeta) \underline{J}_i^{(2)} \cdot \nabla_{Ri} \underline{u}_i. \quad (2.1.12E)$$

Since $\underline{J}_i^{(2)}$, $\rho^{(2)}$, and $\rho^{(1)}$ are the quantities averaged over the velocity space $(\underline{v}_1, \underline{v}_2)$, it may be said that these quantities are in the hydrodynamical level in the 6-dimensional space $(\underline{R}_1, \underline{R}_2)$, i.e. the relaxation time t_r of $\rho^{(2)}$ is in the order of the time interval of a significant hydrodynamical change. Since the mean free path time between collisions t_{mfp} is usually much smaller than the hydrodynamical relaxation time t_r /COH/, the first term of Eq.(2.1.12E) is negligible comparing with $\underline{J}_i^{(2)}$, and we have

$$O_i \approx - (m/\zeta) \underline{J}_i^{(2)} \cdot \nabla_{Ri} \underline{u}_i. \quad (2.1.12F)$$

In liquids as a good approximation we may neglect the effect of dilatation, i.e. $\nabla_{Ri} \cdot \underline{u}_i \approx 0$. The remaining significant contribution comes from the shear rate. Since, however, the quantity $m/\zeta \approx t_{mfp}$ is very small in liquids, the r.h.s. of (2.1.12F) is still small for the shear rate which is not so large. Thus we assume

$$| (m/\zeta) \nabla_{Ri\mu} \underline{u}_{iv} | \ll 1 \quad (2.1.12G)$$

for all $\mu, v (=1,2,3$: Cartesian components) in order to throw out the term O_i . With the assumption (2.1.12G) Eq.(2.1.12F) becomes

$$O_i \approx 0. \quad (2.1.12H)$$

Thus the first-order approximation for $\underline{J}_i^{(2)}$ in ζ^{-1} , given by eq.(2.1.11), may be well justified.

Substitution of $\underline{j}_i^{(2)}$ from Eq. (2.1.11) into the equation of continuity (2.1.3) leads to

$$\begin{aligned} & \partial \rho^{(2)} / \partial t + \nabla_{\underline{R}_1} \cdot (\underline{u}_1 \rho^{(2)}) + \nabla_{\underline{R}_2} \cdot (\underline{u}_2 \rho^{(2)}) \\ & + (1/\zeta) \sum_{i=1}^2 \nabla_{\underline{R}_i} \cdot (-k_B \nabla_{\underline{R}_i} (T_i \rho^{(2)}) + \rho^{(2)} (\underline{F}_i - m \dot{\underline{u}}_i)) \\ & = 0, \end{aligned} \quad (2.1.13)$$

where $\dot{\underline{u}}_i := \partial \underline{u}_i / \partial t + \underline{u}_i \cdot \nabla_{\underline{R}_i} \underline{u}_i$. This is the extended K-S equation for the pair-distribution function $\rho^{(2)} = \rho^{(2)}(\underline{R}_1, \underline{R}_2)$ in 6-dimensional configuration space, where the term nonlinear in the flow velocity $\underline{u}_i$ and the time derivative term $\partial \underline{u}_i / \partial t$ are preserved, and the spatial dependence of the temperature is not excluded. It is a really reasonable result that the mean force $\underline{F}_i$ is to be subtracted by the inertial force $m \dot{\underline{u}}_i$ in the above equation, since the accelerated molecule at $\underline{R}_i$ in the direction of $\underline{F}_i$ sees practically the effective force $(\underline{F}_i - m \dot{\underline{u}}_i)$!

The equation for the pair-correlation function $g(\underline{R}_1, \underline{R}_2)$ defined by

$$\rho^{(2)} =: \rho^{(1)}(\underline{R}_1) \rho^{(1)}(\underline{R}_2) g(\underline{R}_1, \underline{R}_2) \quad (2.1.14)$$

is to be derived from eq. (2.1.13), with which one can calculate the potential contribution to the pressure tensor. From now on the temperature and the molecular number density are assumed to be homogeneous:

$$\begin{aligned} T_1 = T_2 &=: T_0 \\ &: \text{homogeneous} \\ \rho^{(1)}(\underline{R}_1) &= \rho^{(1)}(\underline{R}_2) =: n_0 \end{aligned} \quad (2.1.15)$$

The most physically suitable flow for this homogeneous system is the Couette-flow defined by

$$\underline{u}_i = \underline{R}_i \cdot \underline{\gamma} ; \quad \underline{\gamma} := \begin{pmatrix} 0 & 0 & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (2.1.16)$$

γ : shear rate independent of $\underline{R}_i$ ($i=1,2$).

In a homogeneous system the pair-correlation function g depends upon the relative coordinate only:

$$g(\underline{R}_1, \underline{R}_2) = g(\underline{R})$$

$$\underline{R} := \underline{R}_1 - \underline{R}_2 . \quad (2.1.17)$$

For the sake of simplicity the mean force $\underline{F}_i$ acting on a molecule at $\underline{R}_i$ is approximated by that in equilibrium, $\underline{F}_i^{\text{eq}}$. From the canonical distribution of molecules in equilibrium it may be easily shown that

$$\underline{F}_i^{\text{eq}} = -k_B T_0 \nabla_{\underline{R}_i} \ln g_0(\underline{R})$$

$g_0(\underline{R})$: equilibrium pair-correlation function,

and so the approximation for $\underline{F}_i$ may be written as

$$\underline{F}_i \approx -k_B T_0 \nabla_{\underline{R}_i} \ln g_0 . \quad (2.1.18)$$

The approximation (2.1.18) becomes exact, when the shear rate goes to the zero limit. Substitution of eqs.(2.1.14-18) into eq.(2.1.13) and making use of the equation of continuity for molecular number density

$$\partial \rho^{(1)}(\underline{R}_i) / \partial t + \nabla_{\underline{R}_i} \cdot \{ \underline{u}_i \rho^{(1)}(\underline{R}_i) \} = 0$$

to cancel the terms of time derivative of $\rho^{(1)}(\underline{R}_i)$, lead to the equation for the pair-correlation function in the relative pair space:

$$\partial g / \partial t + \underline{R} \cdot \left(\underline{\gamma} - (m/\zeta) \frac{\partial \underline{\gamma}}{\partial t} \right) \cdot \nabla_R g - (2k_B T_0 / \zeta) \nabla_R \cdot \left(\nabla_R g + (k_B T_0)^{-1} g \nabla_R w \right) = 0, \quad \text{where} \quad (2.1.19)$$

$w := -k_B T_0 \ln g_0$ is the potential of mean force in the relative pair space in equilibrium.

The term nonlinear in $\underline{u}_i$ has vanished identically. The molecular number density n_0 , the temperature T_0 , and the shear rate are homogeneous but can change in the course of time.

Except for the time derivative term of shear rate, $(m/\zeta) \frac{\partial \underline{\gamma}}{\partial t}$, this is formally the same equation as the one that Kirkwood derived in 1949 to calculate the potential contribution to the pressure tensor /KIR2,RIC/. But it should be noticed that the linearization of the flow velocity $\underline{u}_i$ has not been used in deriving eq.(2.1.19). The disappearance of the term nonlinear in $\underline{u}_i$ is purely due to the property of the Couette-flow, while in the Kirkwood's equation the linearization is introduced under the assumption of a small flow velocity. This implies that eq.(2.1.19) is applicable to a fluid system in Couette-flow not only of small shear rate, but also of large shear rate, whereas the equation derived through linearization of flow velocity is restricted to a fluid system of small shear rate and velocity in its own reasoning.

In an oscillating Couette-flow, the time derivative term of shear rate, $(m/\zeta) \frac{\partial \underline{\gamma}}{\partial t}$, which is caused by the inertial term $m \underline{\dot{u}}_i$ in the extended K-S-eq. for $\rho^{(2)}$, (2.1.13), will contribute to the nonequilibrium pair-correlation function g and the dependence of viscosity coefficients on the frequency.

In a stationary case, the molecular number density, the temperature, and the shear rate are constant, and so eq.(2.1.19) becomes

$$\underline{R} \cdot \underline{\dot{\gamma}} \cdot \nabla_R g - D \nabla_R \cdot (\nabla_R g + (k_B T_0)^{-1} g \nabla_R w) = 0$$

$$D := 2k_B T_0 / \zeta: \quad \text{diffusion coefficient.} \quad (2.1.20)$$

Remark

The points in obtaining the closed equation (2.1.13) for $\rho^{(2)}$ are the introduction of the first order approximation for $\underline{J}_i^{(2)}$ in ζ^{-1} , (2.1.11), and its validity discussed in (2.1.12A-H). In the extended K-S-eq. (2.1.13) for $\rho^{(2)}$ the temperature, molecular number density, and the flow velocity may include the spatial dependence as well as the time dependence. It is very important to preserve and show the nonlinear term $\underline{u}_i \cdot \nabla_{Ri} \underline{u}_i$ explicitly, which is neglected in the earlier works from the beginning of the derivation of the equation /KIR2, RIC/, in understanding the applicability of the equation to a fluid system of large shear rate. The operator $\underline{u}_i \cdot \nabla_{Ri}$ is the differentiation in the direction of flow velocity and so the term $\underline{u}_i \cdot \nabla_{Ri} \underline{u}_i$ vanishes identically not only in the Couette flow but also in the laminar flow which is regular and consists of the flow lines with uniform velocity along each line. If one assumes simply the homogeneity of the temperature in this laminar flow, although it is not true in general, the equation (2.1.19) with the spatial dependence of the shear-rate tensor $\underline{\dot{\gamma}}$ can be used also for this kind of flow.

The inertial term $m \ddot{\underline{u}}_i$ in the extended K-S-eq. (2.1.13) will become significant in a rapidly oscillating Couette-flow. In this situation one should subtract the inertial force $m \ddot{\underline{u}}_i$ from the mean force due to the intermolecular interactions in order to obtain the correct force which a test molecule experiences in the time-varying(hydrodynamically!) fluid system effectively.

2.2) Perturbation expansion with respect to the deformation, boundary conditions, and reduction of the system of equations

Before the analysis of the extended K-S-eq. (2.1.19) for g in Couette flow it is convenient to scale the length in the unit of the effective diameter of molecules which will be introduced in the section 3.1). An abbreviation for $k_B T_0$ is also introduced:

$\underline{r} := \underline{R}/\sigma$: reduced coordinate vector

$T_* := k_B T_0$

σ : effective diameter of a molecule (2.2.1)

The diffusion coefficient D is of the dimension (cm^2/sec) and may be written in the following way:

$$D = \sigma^2/\tau, \quad (2.2.2)$$

where τ is related to the relaxation time of the pair-correlation function g . On introducing the definitions (2.2.1-2) into the extended K-S equation (2.1.19) for g , one obtains

$$\partial g / \partial t + \underline{r} \cdot (\underline{\gamma} - (m/\zeta) \partial \underline{\gamma} / \partial t) \cdot \nabla g - \tau^{-1} \nabla \cdot (\nabla g + T_*^{-1} g \nabla w) = 0$$

$$\nabla := \partial / \partial \underline{r}, \quad (2.2.3)$$

especially in a stationary situation the above equation has the following form:

$$\nabla^2 g + T_*^{-1} (\nabla w) \cdot \nabla g + T_*^{-1} (\nabla^2 w) g - \underline{r} \cdot (\underline{\tau} \underline{\gamma}) \cdot \nabla g = 0. \quad (2.2.4)$$

Here the stationary equation (2.2.4) only is considered and the purpose is to calculate the deviation of the nonequilibrium pair-correlation function g from its equilibrium value g_0 pro-

vided g_0 is known. The functional form of g_0 will be examined in detail in the section 3.2). This deviation of g from equilibrium is due to the shear flow. When the shear rate γ is set to be zero, the solution of the stationary equation (2.2.4) becomes the equilibrium pair-correlation function $g_0 = e^{-w/T^*}$. This can be tested by substitution.

The shear-rate tensor $\underline{\gamma}$ may be decomposed into two parts:

$$\underline{\gamma} = \gamma_d \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} - \gamma_r \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\gamma_d = \gamma_r = \gamma/2 \text{ (in the Couette-flow with shear rate } \gamma), \quad (2.2.5)$$

where the first term (symmetric tensor) is associated with the deformation effect of the shear flow on the fluid system and the second term (antisymmetric tensor) causes a rotational effect /HES2,EHH/.

As can soon be seen, the decomposition (2.2.5) is the key point in obtaining a wide variety of functional dependence of the solution for $g(r)$ on the shear rate, where the rotational parameter γ_r plays an important role. Moreover, since the deformation parameter γ_d and the rotational parameter γ_r are two different physical quantities, they may be handled as independent parameters. With the values of $\gamma_d = 0$ and $\gamma_r \neq 0$ one obtains the circular flow rotating about z -axis, for example. Thus the fourth term of shear flow in eq. (2.2.4) is to be separated into its deformation and its rotation part with the decomposition (2.2.5) as follows:

$$\begin{aligned} \underline{r} \cdot (\underline{\tau}_{\underline{\gamma}}) \cdot \nabla g &= (\tau_{\gamma_r}) (\gamma \partial / \partial x - x \partial / \partial y) g + (\tau_{\gamma_d}) (\underline{r} \cdot \underline{\sigma}) \cdot \nabla g \\ &= - (\tau_{\gamma_r}) (\partial g / \partial \phi) + (\tau_{\gamma_d}) (\underline{r} \cdot \underline{\sigma}) \cdot \nabla g, \end{aligned} \quad (2.2.6)$$

where

ϕ : the azimuthal angle in polar coordinates

$$\underline{\underline{\sigma}} := \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

These two terms have different effects on the deviation of the nonequilibrium pair-correlation function g from its equilibrium value g_0 . The equation for the deviation factor ψ defined by

$$g = g_0 (1 + \chi)$$

$$\chi = g_0^{-1/2} \psi \quad (2.2.7)$$

can be derived by substitution of (2.2.7) into eq.(2.2.4):

$$\begin{aligned} & \left(\nabla^2 + (2T_\star)^{-1} \nabla^2 w - (w'/2T_\star)^2 + (\tau \gamma_r) \partial/\partial \phi \right) \psi \\ &= (\tau \gamma_d) \left(-T_\star^{-1} (xy/r) w' \psi + \underline{\underline{\sigma}} \cdot \nabla \psi + 4(xy/r) (g_0^{1/2})' \right) \\ f' &:= df/dr \quad \text{for any radial function } f. \end{aligned} \quad (2.2.8)$$

Here the shear flow term is decomposed according to (2.2.6). The factor in front of ψ , $g_0^{-1/2}$ in (2.2.7), is added for the following two advantages: Firstly, the differential operator without the last term of azimuthal differentiation in the left-hand side of the eq.(2.2.8) becomes hermitian under some homogeneous boundary conditions, which is very useful for the process for the solutions of the equation. Secondly, as one can see in (2.2.8), the inhomogeneous term is small over the whole range of the radial variable r except for $r=1$, whereas in the equation for $\chi = g_0^{-1/2} \psi$ the inhomogeneous term blows up for small values of r , if one has established the equation. The inhomogeneous term in eq.(2.2.8) includes the deformation parameter γ_d only and the smallness of the inhomogeneous term

over the whole range of $r(r \neq 1)$ provides us with a good reason for the perturbation expansion of the equation with respect to γ_d , though the convergence of the expansion is here simply assumed. The deviation factor ψ is expanded in the deformation parameter multiplied by the relaxation time, $(\tau\gamma_d)$, as a perturbation parameter:

$$\psi = \sum_{n=0}^{\infty} \psi_n (\tau\gamma_d)^n. \quad (2.2.9)$$

On substituting (2.2.9) into eq.(2.2.8) and comparing the perturbation coefficients $\{\psi_n : n=0,1,2,\dots\}$ in each power of $(\tau\gamma_d)$, one obtains the following hierarchy of differential equations for $\{\psi_n\}$:

$$\begin{aligned} (\hat{L} + (\tau\gamma_r)\partial/\partial\phi)\psi_0 &= 0 \\ (\hat{L} + (\tau\gamma_r)\partial/\partial\phi)\psi_1 &= 4(xy/r)(g_0^{1/2})' + \hat{M}\psi_0 \\ (\hat{L} + (\tau\gamma_r)\partial/\partial\phi)\psi_{n+1} &= \hat{M}\psi_n \quad \text{for } n \geq 1, \end{aligned}$$

where

$$\begin{aligned} \hat{L} &:= \nabla^2 + (2T_\star)^{-1} \nabla^2 w - (w'/2T_\star)^2 \\ \hat{M} &:= \underline{r} \cdot \underline{g} \cdot \nabla - T_\star^{-1} (xy/r) w'. \end{aligned} \quad (2.2.10)$$

The equations (2.2.10) are not ready to be solved. But for the azimuthal differentiation term $(\tau\gamma_r)\partial/\partial\phi$, the homogeneous equation corresponding to eqs.(2.2.10) could be separable, since the effective potential w is a radial function. So each ψ_n is expanded again in the Fourier-series in the azimuthal angle ϕ as follows:

$$\psi_n = \sum_{m=-\infty}^{\infty} \psi_n^{(2m)}(r, \theta) e^{i2m\phi} \quad \text{for integer } n \geq 0, \quad (2.2.11)$$

where use is made of the symmetry of the Couette-flow, i.e.

$$\psi_n(r, \theta, \phi) = \psi_n(r, \theta, \phi + \pi) \quad \text{for } n \geq 0, \quad (2.2.12)$$

which can be easily checked in eqs.(2.2.10).

The Fourier expansion (2.2.11) is substituted into eqs.(2.2.10) and the rectangular coordinates are transformed into the polar coordinates making use of the following relations/GAS/:

$$\partial/\partial x = \sin \theta \cos \phi \partial/\partial r + r^{-1} \cos \theta \cos \phi \partial/\partial \theta - r^{-1} \sin \phi / \sin \theta \partial/\partial \phi$$

$$\partial/\partial y = \sin \theta \sin \phi \partial/\partial r + r^{-1} \cos \theta \sin \phi \partial/\partial \theta + r^{-1} \cos \phi / \sin \theta \partial/\partial \phi$$

$$\partial/\partial z = \cos \theta \partial/\partial r - r^{-1} \sin \theta \partial/\partial \theta,$$

for the transformation of the following differential operator

$$\underline{r} \cdot \underline{\sigma} \cdot \nabla = x \partial/\partial y + y \partial/\partial x.$$

Other transformations can be performed without difficulty. After a little tedious calculation and on comparing the Fourier components one arrives at another hierarchy of differential equations for $\{\psi_n^{(2m)}\}$:

$$(\hat{L}_r + r^{-2} \hat{L}_\theta + i(2m\tau\gamma_r)) \psi_0^{(2m)}(r, \theta) = 0 \quad (2.2.13A)$$

$$(\hat{L}_r + r^{-2} \hat{L}_\theta + i(2m\tau\gamma_r)) \psi_1^{(2m)}(r, \theta) = (\delta_{m,1} - \delta_{m,-1}) (-i \sin^2 \theta) r (g_0^{1/2}) + i(m-1-\hat{N}) \psi_0^{(2m-2)}(r, \theta) + i(m+1+\hat{N}) \psi_0^{(2m+2)}(r, \theta) \quad (2.2.13B)$$

$$(\hat{L}_r + r^{-2} \hat{L}_\theta + i(2m\tau\gamma_r)) \psi_{n+1}^{(2m)}(r, \theta) = i(m-1-\hat{N}) \psi_n^{(2m-2)}(r, \theta) + i(m+1+\hat{N}) \psi_n^{(2m+2)}(r, \theta) \quad \text{for } n \geq 1, \quad (2.2.13C)$$

where

$$\begin{aligned}\hat{L}_r &:= r^{-2} \partial / \partial r (r^2 \partial / \partial r) + (2T_*)^{-1} \nabla^2 w - (w' / 2T_*)^2 \\ &= r^{-2} \partial / \partial r (r^2 \partial / \partial r) + (2T_*)^{-1} w'' + T_*^{-1} w' / r - (w' / 2T_*)^2\end{aligned}$$

$$\hat{L}_\theta := \sin^{-1} \theta \partial / \partial \theta (\sin \theta \partial / \partial \theta) - 4m^2 / \sin^2 \theta$$

$$\hat{N} := -(4T_*)^{-1} r w' \sin^2 \theta + 2^{-1} \sin^2 \theta r \partial / \partial r + 4^{-1} \sin 2\theta \partial / \partial \theta$$

$$\delta_{m,n} : \text{Kronecker } \delta\text{-symbol.} \quad (2.2.13D)$$

The hierarchy of differential equations (2.2.13A-C) looks very complicated. But through the hermitian property of the differential operator $(\hat{L}_r + r^{-2} \hat{L}_\theta)$ with the corresponding boundary conditions for $\psi_n^{(2m)}(r, \theta)$, it can be reduced to a simple system in which only a few members of $\psi_n^{(2m)}(r, \theta)$ survive for the first or the second order perturbation theory ($n=1, 2$).

Boundary conditions and reduction of the system of differential equations (2.2.13A-C)

As will be discussed in the next chapter, the repulsive part of the realistic intermolecular potential is replaced by an effective hard wall. Hence, practically the boundary surface in the relative pair space consists of the infinite sphere and the effective hard sphere of radius σ . The excess probability current density $/KIR, RIC/$ may be defined by

$$\rho^{(1)}(R_1) \rho^{(1)}(R_2) j_{12} := j_1^{(2)} - j_2^{(2)} \text{ in relative pair space,}$$

and becomes for an uniform system of the Couette flow, from (2.2.3)

$$j_{12} = -\tau^{-1} (\nabla g + T_*^{-1} g \nabla w) \quad (2.2.14)$$

in relative pair space, where the equilibrium approximation for

the mean forces (2.1.18) and the definitions (2.2.1-2) are introduced. When two molecules at $\underline{R}_1$ and $\underline{R}_2$ are separated by a large distance, the presence of one molecule is ignored by another, which implies not only

$$\underline{j}_i^{(2)} \rightarrow 0 \quad \text{for } i = 1, 2 \quad \text{as } |\underline{R}_1 - \underline{R}_2| \rightarrow \infty,$$

but also

$$\underline{j}_1^{(2)} \rightarrow \underline{j}_2^{(2)} \quad \text{as } |\underline{R}_1 - \underline{R}_2| \rightarrow \infty.$$

Therefore the excess probability current density vanishes at the infinite surface:

$$\lim_{r \rightarrow \infty} \underline{j}_{12} = 0. \quad (2.2.15A)$$

When two molecules at $\underline{R}_1$ and $\underline{R}_2$ are in contact at their hard walls, it is clear that the normal components of the excess probability current densities at $\underline{R}_1$ and $\underline{R}_2$ to the hard sphere at the point of contact should be equal to each other:

$$(\underline{j}_1^{(2)})_r = (\underline{j}_2^{(2)})_r \quad \text{if } |\underline{R}_1 - \underline{R}_2| = \sigma$$

(the subscript "r" means the radial component of each vector).

Therefore the radial component of the excess probability current density should vanish at $r = 1$ in the reduced relative pair space:

$$(\underline{j}_{12})_r = 0 \quad \text{at } r = 1. \quad (2.2.15B)$$

On substituting (2.2.7), (2.2.9), and (2.2.11) for g , ψ , and ψ_n respectively, into (2.2.14) for $\underline{j}_{12}$, the boundary conditions (2.2.15A,B) may be rewritten in terms of the Fourier components $\{\psi_n^{(2m)}(r, \theta)\}$ explicitly as follows:

$$\begin{aligned} \lim_{r \rightarrow \infty} \{ \hat{x} g_0 \partial / \partial r \{ g_0^{-1/2} \psi_n^{(2m)}(r, \theta) \} \\ + \hat{\theta} g_0 r^{-1} \partial / \partial \theta \{ g_0^{-1/2} \psi_n^{(2m)}(r, \theta) \} + \hat{\phi} i 2 m r^{-1} g_0^{1/2} \psi_n^{(2m)}(r, \theta) \} = 0 \\ g_0 \partial / \partial r \{ g_0^{-1/2} \psi_n^{(2m)}(r, \theta) \} = 0 \quad \text{at } r = 1, \text{ respectively.} \end{aligned}$$

Since $\lim_{r \rightarrow \infty} g_0(r) = 1$ and the limits of the θ - and ϕ -component in the first relation vanish if the limit of the radial component is zero at infinity, the boundary conditions above are simplified by

$$\begin{aligned} \lim_{r \rightarrow \infty} (g_0 \partial (g_0^{-1/2} \psi_n^{(2m)}) / \partial r) \\ = \lim_{r \rightarrow \infty} \{ (2T_*)^{-1} w' \psi_n^{(2m)} + \partial \psi_n^{(2m)} / \partial r \} = 0 \quad \text{and} \quad (2.2.16A) \end{aligned}$$

$$\begin{aligned} g_0 \partial (g_0^{-1/2} \psi_n^{(2m)}) / \partial r \\ = g_0^{1/2} \{ (2T_*)^{-1} w' \psi_n^{(2m)} + \partial \psi_n^{(2m)} / \partial r \} = 0 \quad \text{at } r = 1, \quad (2.2.16B) \end{aligned}$$

where $g_0 = e^{-w/T_*}$ is used, and m and n ($\geq |2m|$) run over all the integers and the nonnegative integer numbers respectively. The conditions (2.2.16A,B) are the mixed form of homogeneous Dirichlet and Neumann boundary conditions /MOR/.

Let G be the Green's function corresponding to the differential operator $(\hat{L}_r + r^{-2} \hat{L}_\theta)$ in the 2-dimensional (r, θ) -space. Then it can be easily shown that the operator $(\hat{L}_r + r^{-2} \hat{L}_\theta)$ becomes hermitian if its eigenfunctions or G satisfy the same boundary conditions (2.2.16A,B) as $\psi_n^{(2m)}(r, \theta)$:

$$\begin{aligned} \int_0^{2\pi} \int_0^\infty G(\hat{L}_r + r^{-2} \hat{L}_\theta) \bar{\psi} r^2 \sin \theta dr d\theta &= \int_0^{2\pi} \int_0^\infty (\hat{L}_r + r^{-2} \hat{L}_\theta) G \bar{\psi} r^2 \sin \theta dr d\theta \\ 01 &01 \\ \int_0^\infty \int_0^{2\pi} (G \sin \theta \partial \bar{\psi} / \partial \theta - \partial G / \partial \theta \sin \theta \bar{\psi}) \big|_{\theta=0}^\pi dr &+ \int_0^\pi \sin \theta (G r^2 \partial \bar{\psi} / \partial r - \partial G / \partial r r^2 \bar{\psi}) \big|_{r=1}^\infty d\theta \\ 1 &0 \end{aligned}$$

where the bar "-" means the complex conjugate.

The second term in the right hand side vanishes identically and the third term disappears also if one demands

$$\begin{aligned} & \lim_{r \rightarrow \infty} (g_0 \partial (g_0^{-1/2} G) / \partial r) \\ & = \lim_{r \rightarrow \infty} ((2T_*)^{-1} w' G + \partial G / \partial r) = 0 \end{aligned} \quad (2.2.17A)$$

and

$$\begin{aligned} & g_0 \partial (g_0^{-1/2} G) / \partial r \\ & = g_0^{1/2} ((2T_*)^{-1} w' G + \partial G / \partial r) = 0 \quad \text{at } r = 1. \end{aligned} \quad (2.2.17B)$$

Thus $(\hat{L}_r + r^{-2} \hat{L}_\theta)$ is hermitian with the boundary conditions (2.2.17A and B).

Since the eigenvalues of the hermitian operator $(\hat{L}_r + r^{-2} \hat{L}_\theta)$ are real and the number $i(2m\tau\gamma_r)$ is purely imaginary, the solution of the following homogeneous differential equation

$$(\bar{L}_r + r^{-2} \hat{L}_\theta + i(2m\tau\gamma_r)) \psi = 0$$

is trivial, i.e. $\psi = 0$. This implies the following reduction of the system of differential equations (2.2.13A-C):

$$(\hat{L}_r + r^{-2} \hat{L}_\theta + i(2m\tau\gamma_r)) \psi_1^{(2m)}(r, \theta) = (\delta_{m,1} - \delta_{m,-1}) (-i \sin^2 \theta) r (g_0^{1/2})', \quad (2.2.18A)$$

$$\begin{aligned} & (\hat{L}_r + r^{-2} \hat{L}_\theta + i(2m\tau\gamma_r)) \psi_{n+1}^{(2m)}(r, \theta) = i(m-1-\hat{N}) \psi_n^{(2m-2)}(r, \theta) \\ & + i(m+1+\hat{N}) \psi_n^{(2m+2)}(r, \theta) \quad \text{for } n \geq 1, \end{aligned} \quad (2.2.18B)$$

where

$$\begin{aligned}
 \psi_0^{(2m)} &= 0 && \text{for all integer } m \\
 \psi_1^{(2m)} &= 0 && \text{if } m \neq -1, 1 \\
 \psi_2^{(2m)} &= 0 && \text{if } m \neq -2, 0, 2 \\
 &\dots\dots\dots && \dots\dots\dots \\
 \psi_n^{(2m)} &= 0 && \text{if } m \neq -n, -n+2, \dots, n-2, n. \quad (2.2.18C)
 \end{aligned}$$

Especially one obtains for the zeroth-, the first-, and the second-order perturbation

$$\begin{aligned}
 \psi_0 &= 0 \\
 \psi_1 &= e^{-i2\phi} \psi_1^{(-2)}(r, \theta) + e^{i2\phi} \psi_1^{(2)}(r, \theta) \\
 \psi_2 &= e^{-i4\phi} \psi_2^{(-4)}(r, \theta) + \psi_2^{(0)}(r, \theta) + e^{i4\phi} \psi_2^{(4)}(r, \theta). \quad (2.2.19)
 \end{aligned}$$

The result $\psi_0 = 0$ is consistent with the fact that the deviation factor ψ should be zero when there is no shear flow.

As one can see in (2.2.18C) and (2.2.19), the infinite Fourier-series for ψ_n has been remarkably simplified. Moreover, as will be given later explicitly for the first-order perturbation, $\psi_n^{(2m)}(r, \theta)$ and $\psi_n^{(-2m)}(r, \theta)$, are complex conjugates of each other, so that ψ_n may be a real function.

III. Process for solutions of the differential equations for the deviation factors

Since the homogeneous equation corresponding to eqs. (2.2.18A, B) is separable, the hierarchy of equations can be solved systematically. For the simplest case, here the first order perturbation $\Psi_1^{(+2)}(r, \theta)$ only is considered. In order to obtain the nonequilibrium deviation factors $\Psi_1^{(+2)}(r, \theta)$ it is necessary to have the explicit functional form of the equilibrium pair-correlation function g_0 to integrate the differential equation (2.2.18A). Until now the correct closed equation for g_0 is not known and the pair-correlation function g_0 is related to the 3-particle correlation function $g_0^{(3)}$ in a similar way to the situation of BBGKY-hierarchy for the nonequilibrium distribution functions. There are various approximate equations for g_0 , e.g. Yvon-Born-Green equation, Kirkwood equation, and Percus-Yevick equation. Even for these approximate equations one has no exact solutions except for one special case, the solution of the Percus-Yevick equation for hard spheres due to Wertheim and Thiele [WER, THI], which will be used as a special case to calculate $\Psi_1^{(+2)}(r, \theta)$. Although the integral representation for the hard-sphere pair-correlation function g_0^{HS} outside the hard core is known and its systematic calculation is possible [WER], it has little practical value for application to the problem considered here. More practically in section 3.2) the Ornstein-Zernike theory for the correlation function in equilibrium [O-Z1] is introduced and their approximation method [ZER, O-Z2] is discussed and improved.

It will be clearly seen at the end of this chapter and in the next chapter that the most important features in nonequilibrium are closely related to the correct functional form of equilibrium pair-correlation function. For all these purposes, first of all, one should have some kind of intermolecular potential which plays fundamental role in all calculations. In the following section an important and useful ansatz for the intermolecular potential is introduced.

3.1) Ansatz for the intermolecular potential

Instead of dividing the intermolecular potential in its positive and its negative part [RIC], Weeks, Chandler, and Andersen (WCA) separated the intermolecular force in its repulsive and its attractive part [WEE]. The latter separation is more reasonable than the former, for the nearest-neighbour molecules don't know the sign of the potential, rather do see the sign of the force. The higher the molecular density is, the more frequently the molecules see the repulsive forces, and the effect of the attractive forces on the pair-correlation function becomes negligible in high densities. As a good approximation the repulsive part of intermolecular potential may be replaced by the hard-sphere potential with an effective diameter, the best determination of which may be found in the work of H.C. Andersen, J.D. Weeks, and D. Chandler [AND]. This determination of the effective diameter of hard sphere (HS) will be introduced. The "effective" hard-sphere diameter, however, won't be calculated in this work. Its determination accompanied with some error in the excess (the potential contribution) Helmholtz free energy of molecular system is introduced to justify the ansatz for the intermolecular potential.

Now one introduces the following ansatz for the intermolecular potential:

$$v(R/\sigma) = v_{\sigma}(R/\sigma) + v_a(R/\sigma),$$

where

$$v_{\sigma}(R/\sigma) \equiv \begin{cases} \infty, & R \leq \sigma \\ 0, & R > \sigma \end{cases}$$

$$v_a(R/\sigma) \equiv \begin{cases} -\epsilon, & R < R_m \\ v_{LJ}(R/\sigma), & R \geq R_m \end{cases} \quad (3.1.1)$$

In the ansatz (3.1.1) $v_{LJ}(R/\sigma)$ is a Lennard-Jones-like potential, and R_m and $-\epsilon$ are the position and the value of minimum of $v_{LJ}(R/\sigma)$ respectively, as can be seen in fig. 3.1.1. The hard-sphere potential $v_{\sigma}(R/\sigma)$ approximates the repulsive part of $v_{LJ}(R/\sigma)$ depicted in Fig. 3.1.1b), effectively.

The important reason for the ansatz of intermolecular potential (3.1.1) is the following: Firstly, the hard-sphere potential provides us with a convenient boundary condition at the hard core. Secondly, the fluid of molecules with the potential (3.1.1) may well be expected to show some true features of the fluid of molecules with the realistic potential $v_{LJ}(R/\sigma)$, if one adjusts the hard-sphere diameter σ to the repulsive part of $v_{LJ}(R/\sigma)$ effectively. This adjustment of the hard-sphere diameter σ may be done according to the following rule [AND]

$$\int \gamma_{\sigma}(R/\sigma) \left[\phi_{\tau}(R) - \phi_{\sigma}(R) \right] d\underline{R} = 0, \quad (3.1.2)$$

where

$$\gamma_{\sigma}(R/\sigma) \equiv g_{\sigma}(R/\sigma) \exp \left\{ v_{\sigma}(R/\sigma)/T_{*} \right\}$$

$$g_{\sigma}(R/\sigma) : \text{equilibrium pair-correlation function} \quad (3.1.2A) \\ \text{for HS with the diameter } \sigma$$

$$\phi_{\tau}(R) \equiv \exp \left\{ - v_{\tau}(R/\sigma)/T_{*} \right\}$$

$$\phi_{\sigma}(R) \equiv \exp \left\{ - v_{\sigma}(R/\sigma)/T_{*} \right\} \quad (3.1.2B)$$

$$v_{\tau}(R/\sigma) : \text{repulsive part of } v_{LJ}(R/\sigma) \text{ depicted} \\ \text{in fig. 3.1.1.}$$

The effective diameter σ determined in this way depends both upon temperature and density. This is chosen in such a manner that the first-order term may vanish identically in the functional Taylor expansion of the excess (the potential contribution) Helmholtz free energy $A(\phi_{\tau})$ with respect to the Boltzmann factor ϕ_{σ} of the hard-sphere potential $v_{\sigma}(R/\sigma)$. Thus Andersen and his coworkers [AND] estimated the error in the excess Helmholtz free energy to be in the order of

$$\frac{\delta^2 A(\phi_{\sigma})}{\delta \phi_{\sigma}(R) \delta \phi_{\sigma}(R')} \left\{ \phi_{\tau}(R) - \phi_{\sigma}(R) \right\} \left\{ \phi_{\tau}(R') - \phi_{\sigma}(R') \right\} d\underline{R} d\underline{R}', \quad (3.1.3)$$

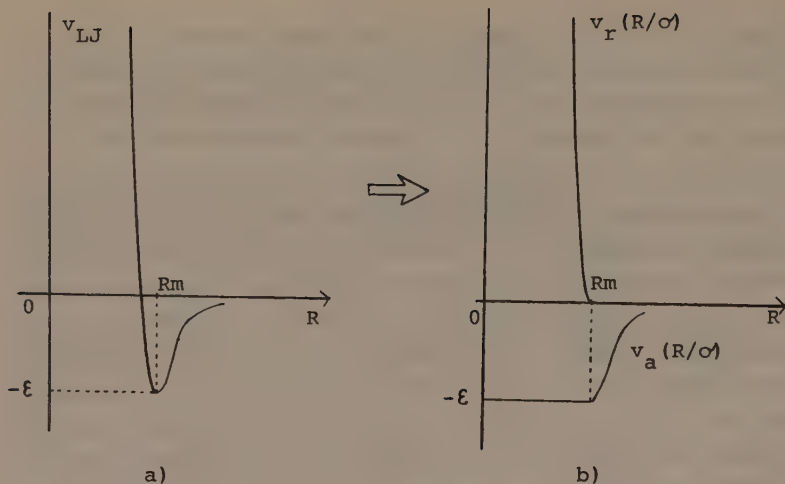


Fig. 3.1.1 a) The Lennard-Jones-like intermolecular potential

b) The WCA-separation of $v(R/\sigma)$ in its repulsive part $v_r(R/\sigma)$ and its attractive part $v_a(R/\sigma)$ [WEE], which are defined as follows:

$$v_r(R/\sigma) = v_{LJ}(R/\sigma) + \epsilon \quad \text{and} \quad v_a(R/\sigma) = -\epsilon \quad \text{for } R < R_m,$$

$$\text{and } v_r(R/\sigma) = 0 \quad \text{and} \quad v_a(R/\sigma) = v_{LJ}(R/\sigma) \quad \text{for } R \geq R_m.$$

when the molecules with the repulsive potential v_r is approximated by the hard spheres with the effective diameter σ .

But how large is the error in the excess Helmholtz free energy, if the realistic intermolecular potential v_{LJ} is approximated by v assumed in (3.1.1)?

This may be seen in the following way. Similarly to the process made in ref. [AND], one may expand the excess Helmholtz free energy of molecules with the potential v_{LJ} in the functional Taylor series with respect to the Boltzmann factor of the potential v given by (3.1.1) as follows

$$\begin{aligned}
 A(\phi_{LJ}) &= A(\phi) + \int \frac{\delta A(\phi)}{\delta \phi(R)} \{ \phi_{LJ}(R) - \phi(R) \} d\underline{R} + \\
 &+ \frac{1}{2} \int \frac{\delta^2 A(\phi)}{\delta \phi(R) \delta \phi(R')} \{ \phi_{LJ}(R) - \phi(R) \} \{ \phi_{LJ}(R') - \phi(R') \} d\underline{R} d\underline{R}' + \\
 &+ \dots,
 \end{aligned} \tag{3.1.4}$$

where $\phi_{LJ} \equiv \exp(-v_{LJ}/T_*)$ and $\phi(R) \equiv \exp(-v/R_*)$.

Since $v = v_\sigma + v_a$ and $v_{LJ} = v_r + v_a$, one has

$$\begin{aligned}
 \phi_{LJ} - \phi &= \exp(-v_a/T_*) \{ \exp(-v_r/T_*) - \exp(-v_\sigma/T_*) \} \\
 &= \exp(-v_a/T_*) \{ \phi_r - \phi_\sigma \},
 \end{aligned} \tag{3.1.4A}$$

and

$$\begin{aligned}
 \frac{\delta A(\phi)}{\delta \phi(R)} &= \int \frac{\delta A(\phi_\sigma)}{\delta \phi_\sigma(R')} \frac{\delta \phi_\sigma(R')}{\delta \phi(R)} d\underline{R}' \\
 &= \int \frac{\delta A(\phi_\sigma)}{\delta \phi_\sigma(R')} \exp\{v_a(R/\sigma)/T_*\} \delta(R - R') d\underline{R}' \\
 &= \frac{\delta A(\phi_\sigma)}{\delta \phi_\sigma} \exp\{v_a(R/\sigma)/T_*\}.
 \end{aligned} \tag{3.1.4B}$$

Substitution of (3.1.4A and B) into (3.1.4) leads to

$$\begin{aligned}
 A(\phi_{LJ}) &= A(\phi) + \int \frac{\delta A(\phi_\sigma)}{\delta \phi_\sigma(R)} \{ \phi_r(R) - \phi_\sigma(R) \} d\underline{R} + \\
 &+ \frac{1}{2} \int \frac{\delta^2 A(\phi_\sigma)}{\delta \phi_\sigma(R) \delta \phi_\sigma(R')} \{ \phi_r(R) - \phi_\sigma(R) \} \{ \phi_r(R') - \phi_\sigma(R') \} d\underline{R} d\underline{R}' + \\
 &+ \dots
 \end{aligned} \tag{3.1.5}$$

The pair-correlation function $g_0(R/\sigma)$ is related to the functional differentiation of the excess Helmholtz free energy with respect to the Boltzmann factor $\phi(R)$ in the following way [RIC, L-P]

$$\begin{aligned}
 \frac{\delta A(\phi)}{\delta \phi(R)} &= -\frac{1}{2} T_* n_0^2 g_0(R/\sigma)/\phi(R) \\
 &= -\frac{1}{2} T_* n_0^2 y(R/\sigma),
 \end{aligned} \tag{3.1.6}$$

where

$$\begin{aligned} y(R/\sigma) &\equiv g_0(R/\sigma)/\phi(R) \\ &= g_0(R/\sigma) \exp\{v(R/\sigma)/T_*\} \end{aligned} \quad (3.1.7)$$

and n_0 : number of molecules per unit volume.

If one substitutes (3.1.6) for the hard-sphere case into (3.1.5) and demands the condition (3.1.2) for the effective diameter σ one obtains finally

$$\begin{aligned} A(\phi_{LJ}) &= A(\phi) + \frac{1}{2} \int \frac{\delta^2 A(\phi_\sigma)}{\delta \phi_\sigma(R) \delta \phi_\sigma(R')} \{ \phi_T(R) - \phi_\sigma(R) \} \{ \phi_T(R') - \phi_\sigma(R') \} dR dR' + \\ &+ \dots \end{aligned} \quad (3.1.8)$$

The difference $(A(\phi_{LJ}) - A(\phi))$ is in the order of the second term of (3.1.8) which is the same given by (3.1.3).

Thus, when the realistic intermolecular potential v_{LJ} is approximated by v assumed in (3.1.1), there occurs the same error in the excess Helmholtz free energy of molecules with the intermolecular potential v_T approximated by the hard-sphere potential v_σ .

The second-order term (3.1.3) becomes very small if one chooses the effective diameter σ according to (3.1.2), and it is in the order of ξ^4 , where ξ is the range of appreciable value of the function $y_\sigma(\phi_T - \phi_\sigma)$ [AND].

3.2) The Ornstein-Zernike approximation for equilibrium density-correlation function with the particular ansatz for intermolecular potential, and its correction and improvement

In equilibrium the Ornstein-Zernike (O-Z) theory for density fluctuation [O-Z1] reads as follows:

$$s(\underline{r}) = c(\underline{r}) + n \int s(\underline{r} - \underline{r}') c(\underline{r}') d\underline{r}' \quad (3.2.1A)$$

or in its Fourier-transformation

$$\tilde{s}(q) = \tilde{c}(q) + n \tilde{s}(q) \tilde{c}(q) \quad (3.2.1B)$$

with n : reduced molecular number density (per the volume σ^3),

where $s(\underline{r})$ and $c(\underline{r})$ are named, density correlation and direct correlation function, respectively, and $\tilde{s}(q)$ and $\tilde{c}(q)$ are their Fourier components, respectively. The density correlation $s(\underline{r})$ is called usually "correlation function" without the preceding noun "density" which is here added to distinguish $s(\underline{r})$ from the equilibrium pair-correlation function $g_0(\underline{r})$. The density correlation function $s(\underline{r})$ is related to $g_0(\underline{r})$ by

$$s(\underline{r}) = g_0(\underline{r}) - 1 \quad (3.2.2)$$

and the former is introduced by Ornstein and Zernike [O-Z1] to explain the influence of density deviation in one volume element on the state in another, and the latter is the measure of frequency that one finds one molecule at $\underline{r}$ in the presence of another at the origin in the reduced relative pair space.

The direct correlation function $c(\underline{r})$ is of very short range (about the range of intermolecular forces) [O-Z1] and its contribution to the integral in eq. (3.2.1A) is significant only for small values of $\underline{r}'$, which implies that one may expand $s(\underline{r}-\underline{r}')$ in the integrand of eq. (3.2.1A) in power series of $\underline{r}'$ and take a few lowest orders to obtain a reasonable

approximation. Thus eq. (3.2.1A) is expanded as follows:

$$\begin{aligned}
 s(r) &= c(r) + n c_0 s(r) + (n/6) c_2 v^2 s(r) + \\
 &+ (n/120) c_4 v^2 v^2 s(r) + \dots \\
 c_{2n} &\equiv \int r^{2n} c(r) dr \quad \text{for } n = 0, 1, 2, \dots, \\
 \text{especially } c_0 &= \tilde{c}(0), \quad (3.2.3)
 \end{aligned}$$

where the integrals containing the odd-power factor in their integrands are missing for the symmetry of equilibrium.

(i) The 0-Z approximation

As frequently made, one can neglect the fourth and the higher derivatives [ZER, 0-Z2, RIC, FIX] in eq. (3.2.3) to obtain the following second-order differential equation for $s(r)$:

$$\begin{aligned}
 v^2 s(r) - v^2 s(r) &= -6 c(r)/(n c_2) \\
 v^2 &\equiv 6 (1 - n c_0)/(n c_2). \quad (3.2.4)
 \end{aligned}$$

Outside the range of intermolecular forces the inhomogeneous term in the right hand side of (3.2.4) is very small and practically the homogeneous solution, satisfying the boundary condition at infinity, is a good approximation for large r . Since for the moment the direct correlation function $c(r)$ is not known and we have seen no way to calculate c_0 and c_2 , the constant v^2 is a phenomenological parameter to be determined under some conditions. Mostly and sometimes tacitly v^2 is considered as a positive constant [ZER, 0-Z2, RIC, FIX, STA] and immediately the homogeneous solution of (3.2.4) is expressed by

$$s(r) = (u/r) e^{-v(r-1)} \quad (v > 0), \quad (3.2.5)$$

where $\tilde{s}(r) \equiv s(r)$ outside the effective hard core ($r > 1$). This is the famous result of O-Z approximation for the density correlation function in the problem of critical opalescence or light (or X-Ray) scattering [O-Z2, STA, S-T].

It is important to notice that the solution (3.2.5) is correct in the following two senses: Firstly, the form of solution (3.2.5) is correct in the sense of "smoothing out" the true solution, i.e. the surface under the curve (3.2.5) being equal to that under the true one, so that the solution (3.2.5) may give the correct value of compressibility, where the fluctuating feature of the true solution (if it has the feature) is ironed out and χ^2 is handled as a phenomenological parameter because the direct correlation function $c(r)$ is not known, as mentioned above. Secondly, the homogeneous solution (3.2.5) is true, if χ^2 has been calculated from the knowledge of functional form of the direct correlation function $c(r)$ and proved to be real positive number.

To see the first case more in detail the solution (3.2.5) is substituted in the compressibility equation [RIC, BAL] given by

$$\begin{aligned} n T_* K_T &= 1 + n \int s(r) d\underline{r} \\ &= 1 + n \int_{r < 1} \tilde{s}(r) d\underline{r} + n \int_{r > 1} \tilde{s}(r) d\underline{r} \\ &= 1 - n \int_{r < 1} d\underline{r} + n \int_{r > 1} \tilde{s}(r) d\underline{r} \\ &= 1 - \frac{4\pi}{3} n + 4\pi n \int_1^\infty \tilde{s}(r) r^2 dr, \end{aligned} \quad (3.2.6)$$

where $\tilde{s}(r) \equiv \{s(r) \text{ for } r \leq 1\} = -1$, since $s(r) = g_0(r) - 1 = -1$ inside the effective hard core. Then χ^2 may be represented in terms of the isothermal compressibility K_T and the proportional coefficient u as follows:

$$\chi^{-1} = -\frac{1}{2} + \sqrt{1 + (n T_* K_T + 4\pi n/3 - 1)/(\pi n u)} \quad , \quad (3.2.7)$$

where another solution for χ^{-1} is abandoned because of the boundary condition for $\tilde{s}(r)$ at infinity. The expression for the correlation length χ^{-1} , (3.2.7), may well be expected to be better than the Fixman's expression [FIX], for he integrated the density correlation function $s(r)$ with the

functional form of (3.2.5), which departs strongly from the true solution within the range of intermolecular force, over the whole range of r , whereas in eq. (3.2.6) the integration inside the effective hard core is considered separately and executed correctly, which is one of the strong points of the ansatz for intermolecular potential (3.1.1). For $n > \frac{3}{4\pi}$ (or $x > 0.125$), $n T_* K_T + 4 \pi n/3 - 1 > 0$. For $n < \frac{3}{4\pi}$, one may put $K_T \approx K_0 = \frac{1}{nT_*}$, where K_0 is the compressibility of ideal gas, and obtains again the inequality $(n T_* K_T + 4 \pi n/3 - 1) \geq 0$.

Thus, if u is positive, v seems to be always real positive number, which implies the validity of the assumption for $\tilde{g}(r)$ (3.2.5), even if it is "smoothed out".

Since there are two parameters, v and u , to be determined, another condition is needed. The most pertinent condition is the pressure equation [RIC, BAL]: In the unit of energy per the volume σ^3 ,

$$p = n T_* - \frac{2}{3} \pi n^2 \int_0^\infty v'(r) g_0(r) r^3 dr.$$

On replacing $v(r)$ by the ansatz (3.1.1) one has

$$p = n T_* - \frac{2}{3} \pi n^2 \int_0^\infty \{v'_\sigma(r) + v'_a(r)\} e^{-(v_\sigma + v_a)/T_*} y(r) r^3 dr,$$

where the function $y(r)$ defined by (3.1.7):

$$y(r) \equiv e^{v(r)/T_*} g_0(r)$$

and assumed to be continuous at the hard core (e.g. $y(r)$, its first, and its second derivative are continuous at $r = 1$ in the Percus-Yevick equation for hard spheres). Since

$$e^{-v_\sigma(r)/T_*} = \begin{cases} 0, & r \leq 1 \\ 1, & r > 1 \end{cases},$$

one finds the following useful Dirac- δ -function expression:

$$\begin{aligned} v_a'(r) e^{-v_a(r)/T_*} &= -T_* \frac{d}{dr} \left\{ e^{-v_a(r)/T_*} \right\} \\ &= -T_* \delta(r-1) . \end{aligned}$$

Then the above expression for p becomes

$$p = n T_* + \frac{2}{3} \pi n^2 T_* e^{-v_a(1)/T_*} \cdot y(1) - \frac{2}{3} \pi n^2 \int_0^{\infty} v_a'(r) g_0(r) r^3 dr ,$$

or more compactly

$$p = n T_* + \frac{2}{3} \pi n^2 T_* g_0(1^+) - \frac{2}{3} \pi n^2 a$$

with

$$a \equiv \int_{R_m/\sigma}^{\infty} v_a'(r) g_0(r) r^3 dr , \quad (3.2.8)$$

where the following two relations:

$$e^{-v_a(1)/T_*} \cdot y(1) = g_0(1^+)$$

and

$$v_a'(r) = 0 \quad \text{for } r < R_m/\sigma , \text{ from (3.1.1)}$$

have been used.

The expression (3.2.8) is a van der Waals-like equation. The last term of (3.2.8) is negative and caused by the attractive forces of molecules. The first and the second term are the ideal-gas part and the effective hard-core contribution respectively and constitute the main portion of pressure. Here one sees another strong point of the particular separation of inter-molecular potential (3.1.1). Since the length is scaled by the effective

hard sphere diameter σ which is dependent upon both density and temperature, the expression (3.2.8) shows in fact much more complicated functional dependence of p on density and temperature than its formal outlook. On neglecting the last term of (3.2.8) in a dense fluid, one obtains a very simple approximate expression for the pressure:

$$p \approx n T_* + \frac{2}{3} \pi n^2 T_* g_0(1^+) , \quad (3.2.9)$$

which becomes exact for the hard-sphere fluid.

Using the relation $g_0(r) = s(r) + 1$ and substitution of $\bar{s}(r)$ from (3.2.5) into the equation (3.2.8) yields the following result for the coefficient u :

$$u = \frac{3}{2\pi n} \left(\frac{p}{nT_*} - 1 \right) + a/T_* - 1 . \quad (3.2.10)$$

The correlation length ν^{-1} can be expressed in terms of K_T and p replacing u in eq. (3.2.7) by the value of (3.2.10) as follows:

$$\nu^{-1} = -\frac{1}{2} + \frac{1}{2} \sqrt{1 + 2(n T_* K_T + 4 \pi n/3 - 1) / \left\{ 3 \left(\frac{p}{nT_*} - 1 \right) + 2 \pi n (a/T_* - 1) \right\}} , \quad (3.2.11)$$

where a is defined in (3.2.8).

For a high temperature the pressure becomes very large in the higher densities and one has a positive value of u in (3.2.10), which implies the positive real value of ν^{-1} in (3.2.11) and the validity of the ansatz (3.2.5) for density correlation function. Below the critical temperature, however, the compressibility factor $p/(nT_*)$ is smaller in the lower- and the middle-density region than unity [BAL]. In this situation one cannot guarantee that u is a positive number in (3.2.10). Contrarily it seems to be negative, since a is a small number. If u is negative, ν^{-1} in (3.2.11) becomes negative or complex number, which implies that the ansatz (3.2.5) is not valid.

Thus one cannot exclude absolutely the possibility that ν^{-1} may be non-real number in (3.2.11). The assumption (3.2.5) is not valid more in this situation. The compressibility and the pressure in the expressions (3.2.11) are not given explicitly and we have seen no way to calculate them. They can be measured directly in the experiments or in the machine calculations or given by the results of some special models, e.g. the P-V equation for hard spheres.

Even if ν^{-1} is positive and the form of solution (3.2.5) allowable, its validity is correct only in the sense of "smoothing out" the true density correlation function.

By all means it is necessary for the correct ansatz for the homogeneous solution of (3.2.4) to consider the sign of ν^2 , which may be deduced from the correct functional form of the direct correlation function $c(r)$. In the next subsection the two situations are considered according to the sign of ν^2 which may be simply assumed without knowing the correct functional form of $c(r)$.

(ii) Correction of the O-Z approximation

The definition of ν^2 in (3.2.4) may be rewritten, using the relations (3.2.18) and (3.2.6)

$$\begin{aligned}\nu^2 &\equiv 6 (1 - n c_0) / (n c_2) = 6 (1 - n \tilde{c}(0)) / (n c_2) \\ &= 6 / \{ (1 + n \tilde{s}(0)) (n c_2) \}\end{aligned}$$

or

$$\nu^2 = (6/c_2) / (n^2 T_* K_T) , \quad (3.2.12)$$

where $n T_* K_T = 1 + n \tilde{s}(0) = \frac{1}{1 - n c_0}$.

As mentioned in the preceding subsection, for the correct homogeneous solution of eq. (3.2.4) one should consider the following two situations: a) $\nu^2 \geq 0$ and b) $\nu^2 < 0$.

a) $\nu^2 \geq 0$

The homogeneous solution may be put in the form of (3.2.5). The constant ν can be determined by the relation (3.2.12), if the direct correlation function $c(r)$ is given, and the proportional constant u by the compressibility equation (3.2.6). Since in most cases the direct correlation function is not known, one may try to determine u and ν rather more easily using some two conditions which the solution (3.2.5) should satisfy. The most pertinent candidates to these conditions are the compressibility and the pressure equation (3.2.6, 8), respectively. At the end of the calculation the sign of ν^2 should be checked whether it belongs to this situation. If $\nu^2 < 0$, the ansatz for solution (3.2.5) is not correct, one should try to find the solution otherwise.

b) $\nu^2 < 0$

The homogeneous solution should be written as

$$\begin{aligned} \bar{z}(r) &= \sum_{l=1}^2 (u_l/r) e^{\nu_l(r-1)} \\ \nu_1 = \bar{\nu}_2 &\equiv i \sqrt{|\nu^2|} = i \sqrt{|6/c_2|/(n^2 T_* K_T)} \quad \text{from (3.2.12)} \\ u_1 &= \bar{u}_2, \end{aligned} \quad (3.2.13)$$

where the bar "-" means the complex conjugate, and the second and the third line follow from the fact that the density correlation function is real. If the direct correlation $c(r)$ is not known, one should have four equations to determine the four parameters ν_1, ν_2, u_1 , and u_2 .

But, with $c(r)$ known one has only to require two conditions for u_1 and u_2 : the compressibility equation (3.2.6) and the pressure equation (3.2.8). In the next subsection the latter case will be considered, for the direct correlation function is known exactly and explicitly for the P-Y equation for hard spheres.

(iii) The case of the P-Y equation for hard spheres

The P-Y equation is exactly solved for hard-sphere system [WER, THI] and the function $y_{\sigma}(r)$ defined by (3.1.2A) is given for the range $r \leq 1$ by

$$y_{\sigma}(r) = y_{\sigma}^{\leq}(r) \quad \text{for } r < 1$$

$$y_{\sigma}^{\leq}(r) = a_0 + a_1 r + a_3 r^3 \quad \text{for } r < 1$$

$$a_0 = (1 + 2x)^2 / (1 - x)^4$$

$$a_1 = -6x(1 + x/2)^2 / (1 - x)^4$$

$$a_3 = \frac{x}{2} (1 + 2x)^2 / (1 - x)^4$$

$$x \equiv \pi n/6 \quad (3.2.14)$$

In the P-Y equation for hard spheres the direct correlation function can be expressed in terms of the function $y_{\sigma}^{\leq}(r)$ [WER] as follows

$$c(r) = \begin{cases} -y_{\sigma}^{\leq}(r) & , \quad r < 1 \\ 0 & , \quad r > 1 \end{cases} \quad (3.2.15)$$

Although it is possible to express the density correlation $s(r)$ in the integral representation, using the O-Z relation (3.2.1A, B) and the explicit functional form of $c(r)$ from (3.2.14, 15), it is very difficult to see the explicit functional form of $s(r)$ for a wide range of r and the integral

representation for $s(r)$ is not practical for the problem of long-range behavior of $s(r)$, for which the truncated second-order differential equation (3.2.4) would be more useful.

Since $c(r) = 0$ for $r > 1$, the differential equation (3.2.4) becomes homogeneous for $r > 1$ and may be rewritten as

$$v^2 \tilde{s}_{PYH}(r) - v^2 \tilde{s}_{PYH}(r) = 0 \quad \text{for } r > 1, \quad (3.2.16)$$

where "PYH" means the P-Y equation for hard spheres. The integrals c_0 and c_2 defined in (3.2.3) can be calculated by using (3.2.14, 15):

$$\begin{aligned} c_0 &\equiv \int c(r) \, d\underline{r} = -4 \pi \int_0^1 v_{\sigma}^{\zeta}(r) r^2 \, dr \\ &= n^{-1} \left\{ 1 - (1 + 2x)^2 / (1 - x)^4 \right\} \\ c_2 &\equiv \int r^2 c(r) \, d\underline{r} = -4 \pi \int_0^1 v_{\sigma}^{\zeta}(r) r^4 \, dr \\ &= -(\pi/20) (16 - 11x + 4x^2) / (1 - x)^4. \end{aligned} \quad (3.2.17)$$

On making use of (3.2.17) and the relation (3.2.12), v^2 can be expressed in terms of the molecular density:

$$\begin{aligned} v^2 &= (6/c_2) / (n^2 T_* K_T) \\ &= - (120/\pi) (1 - x)^4 / \left\{ (16 - 11x + 4x^2) (n^2 T_* K_T) \right\} \\ &= - (20/x) (1 + 2x)^2 / (16 - 11x + 4x^2), \end{aligned} \quad (3.2.18)$$

where $n T_* K_T = (1 - n c_0)^{-1} = (1 - x)^4 / (1 + 2x)^2$.

The maximum value of x is the closest-packed density, $x_{c.p.} = \pi \sqrt{2}/6$, and the value of x is physically allowable only in the range:

$$0 \leq x < x_{c.p.} = \pi \sqrt{2}/6 = 0.740... \quad (3.2.19)$$

Within this range of x , v^2 is always negative! This can be seen in (3.2.18), and the solution of (3.2.16) should be put in the form of (3.2.13):

$$\begin{aligned} s_{PYH}^{\sim}(r) &= \sum_{l=1}^2 (u_l/r) e^{v_l(r-1)} \\ v_1 &= \bar{v}_2 = i v_0 \\ v_0 &\equiv \sqrt{20} (1 + 2x) / \sqrt{x (16 - 11x + 4x^2)} \\ u_1 &= \bar{u}_2 . \end{aligned} \quad (3.2.20)$$

One now has only to determine the two coefficients u_1 and u_2 , for which the compressibility equation (3.2.6) and the pressure equation (3.2.8) will be used. In the representation for $s_{PHY}^{\sim}(r)$ there is no exponential damping factor, which appears in the exact solution of P-Y equation [WER] in the following way:

$$\sum_1 \left\{ (A_1/r) e^{(\xi_1 + i y_1)r} + (\bar{A}_1/r) e^{(-\xi_1 - i y_1)r} \right\} \quad \text{with all } \xi_1 > 0, \quad (3.2.21)$$

where A_1 and $\bar{A}_1$, and $(-\xi_1 + i y_1)$ and $(-\xi_1 - i y_1)$ appear as pairs of complex conjugates, because the poles of the integrand of the integral representation for $s_{PYH}^{\sim}(r)$ occur in pairs of complex conjugate, but the determination of their positions is not easy. The pair of terms with the smallest ξ_1 in (3.2.21) determines the asymptotic behavior of $s_{PYH}^{\sim}(r)$ for large r . Since without the exponential damping factor one cannot substitute $s_{PYH}^{\sim}(r)$ into the compressibility equation (3.2.6), an ad hoc recipe should be introduced: The expression (3.2.20) may be rewritten in the following form with the exponential damping factor:

$$s_{PYH}^{\sim}(r) = \sum_{l=1}^2 (u_l/r) e^{(-\xi + v_l)(r-1)} \quad (\xi > 0) . \quad (3.2.20)'$$

The real positive constant ϵ is formally introduced for the convergence of the integral and it is to be put to zero after integration. The modified form of $\bar{s}_{PYH}(r)$ is substituted into the compressibility equation (3.2.6), which leads to the following relation:

$$\begin{aligned} n T_* K_T &= 1 - \frac{4\pi}{3} n + 4\pi n \int_1^{\infty} \bar{s}_{PYH}(r) r^2 dr \\ &= 1 - \frac{4\pi}{3} n + 4\pi n \sum_{l=1}^2 u_l \int_1^{\infty} e^{(-\epsilon + v_l)(r-1)} r dr \\ &= 1 - \frac{4\pi}{3} n + 4\pi n \sum_{l=1}^2 u_l \left\{ (\epsilon - v_l)^{-1} + (\epsilon - v_l)^{-2} \right\} \end{aligned}$$

or, after taking the limit $\epsilon \rightarrow 0$,

$$u_1 (v_1^{-2} - v_1^{-1}) + u_2 (v_2^{-2} - v_2^{-1}) = (n T_* K_T + 8x - 1)/(24x), \quad (3.2.22)$$

where the relation $x = \pi n/6$ is used, and $n T_* K_T$ and $v_{1,2}$ are given by (3.2.18, 20), respectively.

Another relation for u_1 and u_2 may be obtained by substituting (3.2.20) into the pressure equation (3.2.8) as follows:

$$n T_* + \frac{2}{3} \pi n^2 T_* y_{\sigma}^{\epsilon}(1) = p = n T_* + \frac{2}{3} \pi n^2 T_* \left\{ \bar{s}_{PYH}(1^+) + 1 \right\},$$

where $v_a = 0$ and the continuity of the function $y_{\sigma}(r)$ at $r = 1$ [WER] is used.

Substituting the exact form of y_{σ}^{ϵ} from (3.2.14) into the left-hand side of the first equation above and the approximated form of $\bar{s}_{PYH}$ from (3.2.20) into the right-hand side of the second equation leads to

$$\begin{aligned} u_1 + u_2 &= a_0 + a_1 + a_3 - 1 \\ &= \frac{1}{2} x (5 - 2x)/(1 - x)^2, \end{aligned} \quad (3.2.23)$$

By the two equations (3.2.22, 23) u_1 and u_2 are determined as follows:

$$u_1 = \bar{u}_2 = \frac{x(5-2x)}{4(1-x)^2} - i \frac{\sqrt{5x}}{120} \frac{170 + 40x - 366x^2 + 256x^3 - 19x^4}{(1-x)^2(1+2x)\sqrt{16-11x+4x^2}} \quad (3.2.24)$$

(iv) The fourth-order approximation

The equation (3.2.4) is the second-order approximation of the O-Z equation (3.2.1A), whose solutions are discussed in the foregoing subsections (i), (ii), and (iii). In order to improve it one can take the next higher-derivative term further in (3.2.3) and obtain the fourth-order partial differential equation:

$$s(r) = c(r) + n c_0 s(r) + (n/6) c_2 \nabla^2 s(r) + (n/120) c_4 \nabla^2 \nabla^2 s(r) \quad (3.2.25)$$

To see the solutions more easily the eq. (3.2.25) may be rearranged as follows:

$$\nabla^2 \left\{ \nabla^2 s(r) - \alpha^2 s(r) \right\} - \beta^2 \left\{ \nabla^2 s(r) - \alpha^2 s(r) \right\} = - \frac{120}{n c_4} c(r) \quad (3.2.25)'$$

where, comparing (3.2.25)' with (3.2.25), α^2 and β^2 should satisfy the following algebraic equations:

$$\alpha^2 + \beta^2 = -20 c_2/c_4$$

$$\alpha^2 \beta^2 = -120 (1 - n c_0)/(n c_4) = - \frac{120}{n^2 T_* K_T c_4} \quad \text{from (3.2.12),}$$

whose solutions are

$$\alpha^2 = -10 c_2/c_4 + \sqrt{(10 c_2/c_4)^2 + 120/(n^2 T_* K_T c_4)}$$

$$\beta^2 = -10 c_2/c_4 - \sqrt{(10 c_2/c_4)^2 + 120/(n^2 T_* K_T c_4)} \quad (3.2.26)$$

The expression (3.2.26) is general. But the special case of the P-Y^{HS} equation (P-Y equation for hard spheres) will be considered from now on in this subsection. It is hoped that the missing exponential decaying factor in the second-order approximation for $\hat{s}_{PVH}(r)$ may be found in the fourth-order approximation for the P-Y^{HS} equation.

In the case of the P-Y^{HS} equation c_0 and c_2 are given by (3.2.17), and c_4 can be easily calculated by using (3.2.14, 15), which results in

$$c_4 = -(\pi/140) (80 - 72 x + 12 x^2 + 7 x^3)/(1 - x)^4 \quad (3.2.27)$$

These values of c_0 , c_2 , and c_4 may be substituted in (3.2.26), which gives the explicit expressions for α^2 and β^2 :

$$\alpha^2 = \left\{ -70 (16 - 11 x + 4 x^2) + i 10 \sqrt{\frac{35}{x}} \sqrt{64 - 160 x + 528 x^2 - 535 x^3 + 184 x^4} \right\}$$

$$/(80 - 72 x + 12 x^2 + 7 x^3)$$

$$\beta^2 = \left\{ -70 (16 - 11 x + 4 x^2) - i 10 \sqrt{\frac{35}{x}} \sqrt{64 - 160 x + 528 x^2 - 535 x^3 + 184 x^4} \right\}$$

$$/(80 - 72 x + 12 x^2 + 7 x^3) \quad , \quad (3.2.28)$$

where the polynomial in the square root is always positive for all the allowed values of x ($0 \leq x < \pi \sqrt{2}/6$), and α^2 and β^2 are complex numbers with the negative real parts and the nonzero imaginary parts. The homogeneous solution of (3.2.25)' may be written as

$$(u/r) e^{\alpha(r-1)} + (\bar{u}/r) e^{\beta(r-1)} + (\beta/r) e^{-\alpha(r-1)} + (\bar{\beta}/r) e^{-\beta(r-1)}, \quad (3.2.29)$$

where $\alpha = \bar{\beta}$ from (3.2.28), and the solution becomes real.

Since $2n\pi + \frac{\pi}{2} < \arg \alpha^2 < 2n\pi + \pi$ and $2n\pi + \pi < \arg \beta^2 < 2n\pi + \frac{3\pi}{2}$ for $n = 0, \pm 1, \pm 2, \dots$, the arguments of the square roots of α^2 and β^2 are confined to the following regions:

$$\begin{aligned} \frac{5\pi}{4} < \arg \alpha < \frac{3\pi}{2} ; \quad \frac{\pi}{4} < \arg (-\alpha) < \frac{\pi}{2} \\ \frac{\pi}{2} < \arg \beta < \frac{3\pi}{4} ; \quad \frac{3\pi}{2} < \arg (-\beta) < \frac{7\pi}{4} \end{aligned} \quad (3.2.30)$$

where $0 \leq \arg z < 2\pi$ for any complex number $z \neq 0$. Then the last two terms in (3.2.29) blow up for large r and should be excluded. The pertinent homogeneous solution of (3.2.25)' to the boundary condition at infinity is

$$s_{PVH}(r) = \sum_{l=1}^2 (u_l/r) e^{v_l(r-1)} \quad (3.2.31)$$

where $u_1 = \bar{u}_2$,

$v_1 = \alpha$ and $v_2 = \beta = \bar{\alpha}$ are given by (3.2.28) with the restrictions (3.2.30).

The two coefficients u_1 and u_2 are determined by the compressibility and the pressure equation (3.2.6, 8). The formalism is similar to that in the subsection (iii) and one obtains two equations for u_1 and u_2 , as in eqs. (3.2.22, 23):

$$\begin{aligned} u_1 (v_1^{-2} - v_1^{-1}) + u_2 (v_2^{-2} - v_2^{-1}) &= (n T_* K_T + \theta x - 1)/(24 x) \\ &= (x/24) (34 + 28 x + x^2)/(1 + 2 x)^2 \end{aligned}$$

$$u_1 + u_2 = a_0 + a_1 + a_3 - 1 = (x/2) (5 - 2 x)/(1 - x)^2,$$

whose solutions are

$$u_1 = \bar{u}_2 = \frac{x}{24} \left\{ \frac{34 + 28 x + x^2}{(1 + 2 x)^2} - (\beta^{-2} - \beta^{-1}) \frac{60 - 24 x}{(1 - x)^2} \right\} / \left\{ \alpha^{-2} - \alpha^{-1} - \beta^{-2} + \beta^{-1} \right\}, \quad (3.2.32)$$

where α and β are obtained from (3.2.28) restricted to (3.2.30).

As hoped in the beginning of this subsection the solution (3.2.31) has the exponential decaying factor and doesn't need the ad hoc recipe for the convergence of the integral for compressibility as in the subsection (iii), which implies that the fourth-order solution (3.2.31) is better in describing the asymptotic behavior of the density correlation function for $r > 1$ than the second-order solution (3.2.20). As will be seen later, it is required in calculating the HS nonequilibrium pair-correlation function even for small r that one should know not only the correct value for the equilibrium pair-correlation function at the hard core (i.e. the correct pressure: see the relation (3.2.9)) but also its correct behavior for $r > 1$.

The forth-order solution for equil. pair-correl. function is displayed for various densities in Fig.(3.2.1) by using (3.2.31) and (3.2.32).

Notation

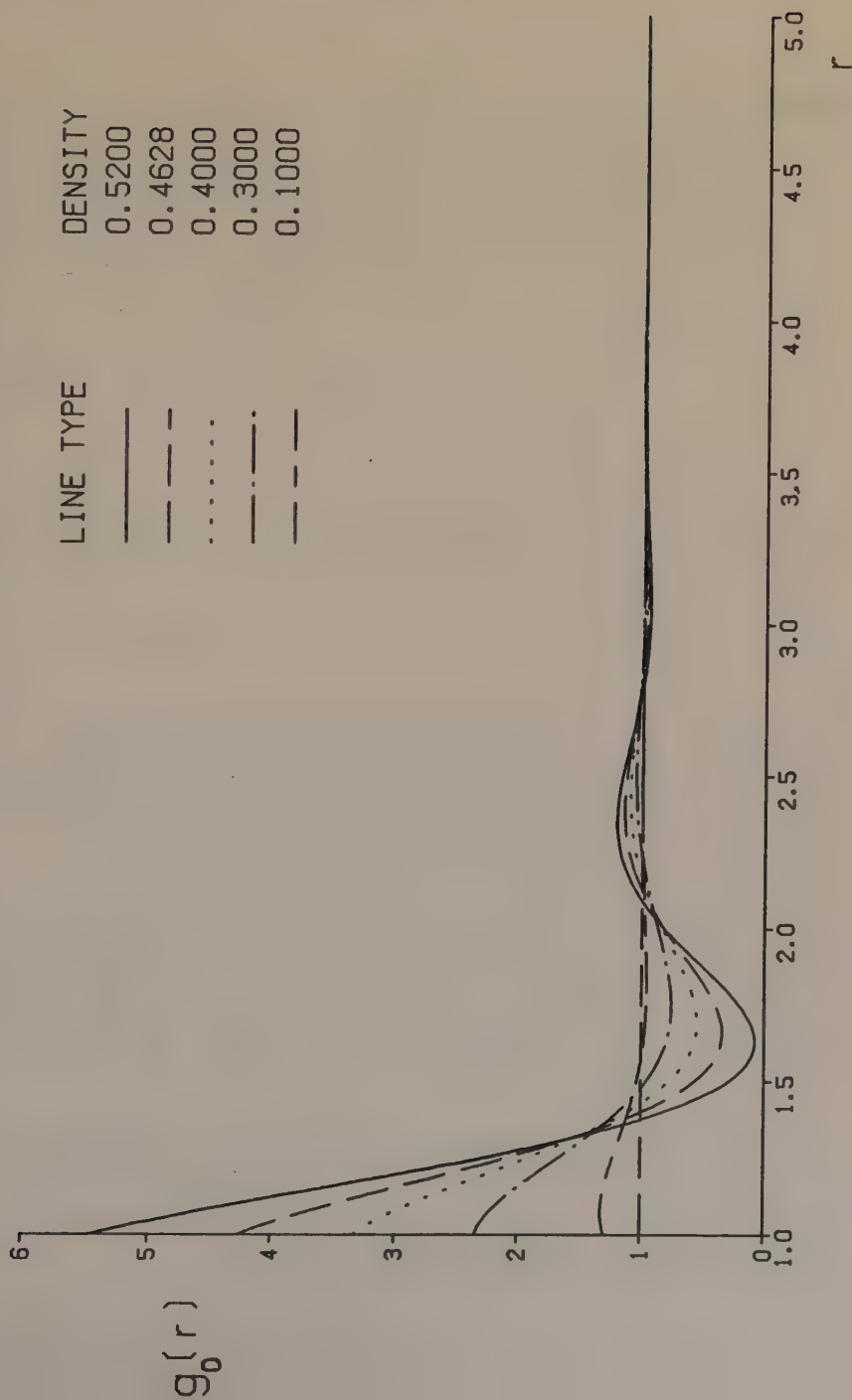
For the later usage it is convenient to introduce a representation for $\tilde{s}(r)$ of the various situations, by writing

$$\tilde{s}(r) = \sum_I^* (u_1/r) e^{\chi_1(r-1)}, \quad (3.2.33)$$

where with "*" replaced by some statement number the summation means the corresponding statement, e.g. $\# := (3.2.31)$ implies that the summation (3.2.33) is replaced by that of (3.2.31), i.e.

$$\sum_I^{(3.2.31)} (u_1/r) e^{\chi_1(r-1)} \equiv \sum_{i=1}^2 (u_1/r) e^{\chi_i(r-1)} \text{ from (3.2.31).}$$

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Remark

By taking the terms to the sixth derivative in eq. (3.2.3) one obtains the sixth-order partial differential equation, which may be rearranged (in the similar way to (3.2.25)') in the following form:

$$\begin{aligned} & \nabla^2 \left[\nabla^2 \left\{ \nabla^2 s(r) - \alpha_1^2 s(r) \right\} - \alpha_2^2 \left\{ \nabla^2 s(r) - \alpha_1^2 s(r) \right\} \right] - \\ & - \alpha_3^2 \left[\nabla^2 \left\{ \nabla^2 s(r) - \alpha_1^2 s(r) \right\} - \alpha_2^2 \left\{ \nabla^2 s(r) - \alpha_1^2 s(r) \right\} \right] = \\ & = (\text{const}) c(r)/c_6 . \end{aligned}$$

This equation is symmetric with respect to the permutation of the three constants α_1, α_2 , and α_3 , and immediately its general form of homogeneous solution may be seen as

$$\frac{u_1}{r} e^{-\alpha_1(r-1)} + \frac{u_2}{r} e^{-\alpha_2(r-1)} + \frac{u_3}{r} e^{-\alpha_3(r-1)} + \frac{u_4}{r} e^{-\alpha_1(r-1)} + \frac{u_5}{r} e^{-\alpha_2(r-1)} + \frac{u_6}{r} e^{-\alpha_3(r-1)} .$$

The terms which are not pertinent to the boundary condition at infinity should be abandoned. If there survive three terms for the $P-V^{\text{HS}}$ equation, the three proportional coefficients of u_1 's may be determined by the three conditions: the compressibility equation, the pressure equation, and the continuity of the first derivative of the density correlation function at the hard core, i.e. $\left\{ \frac{d}{dr} \bar{y}_0(r) \right\}_{r=1} = \left\{ \frac{d}{dr} (\bar{s}(r) + 1) \right\}_{r=1+}$. If there survive four terms, the matching condition of continuity of the second derivative of density correlation function at $r = 1$, i.e. $\left\{ \frac{d^2}{dr^2} \bar{y}_0(r) \right\}_{r=1} = \left\{ \frac{d^2}{dr^2} (\bar{s}(r) + 1) \right\}_{r=1+}$ can be added, since the function $y_0(r) \equiv \exp(v_0(r)/T) g_0(r)$ and its first and second derivative are continuous at the hard core [WER].

This sixth-order solution will describe well not only the asymptotic behaviour for large r , but also the correct form of density correlation function near the hard core, for the values of the function, its first, and its second derivative at the hard core are considered correctly.

The similar process can be made further for the higher order partial differential equation obtained from (3.2.3), where one should have more conditions to determine the constants. When the direct correlation function is known, the number of constants to be determined is reduced to the half of the number of constants to be determined without knowing it. But one should solve the higher order algebraic equation, as was done in (3.2.26).

3.3) Solutions for the deviation factor χ

One now is prepared to start solving the differential equations (2.2.18A,B) for the deviation factors. In this work, however, only the equation of first-order perturbation (2.2.18A) will be treated, which doesn't lose the essential feature of the physics, as will be discussed later. The higher-order perturbations may be obtained hierarchically by using the equations (2.2.18B), where the same mathematical formalism is applied as in the case of first-order perturbation. In the first subsection the general expression for the deviation factor of first-order perturbation will be obtained. In the second subsection this general solution will be shown explicitly by using the improved O-Z approximation for the equilibrium correlation function described in the last section. Especially the solution for the hard-sphere system will be obtained in its complete explicit form, which enables us to calculate the viscosity coefficients for hard spheres explicitly.

(i) The general solution

The starting point in this section is eq. (2.2.18A), which can be rewritten showing the operator $\hat{L}_r$ from (2.2.13D) explicitly:

$$\begin{aligned} & \left(r^{-2} \partial / \partial r (r^2 \partial / \partial r) + V(r) + r^{-2} \hat{L}_\theta + i(2m\tau\gamma_r) \right) \psi_1^{(2m)}(r, \theta) \\ & = (-im \sin^2 \theta) r (g_0^{1/2})', \end{aligned} \quad (3.3.1)$$

where $m = \pm 1$

$$\begin{aligned} V &:= -g_0^{-1/2} v^2 g_0^{1/2} \\ &= w' / (rT_\star) + w'' / (2T_\star) - (w' / 2T_\star)^2 \end{aligned}$$

and $\hat{L}_\theta$ is defined in (2.2.13D).

To solve the inhomogeneous partial differential equation (3.3.1) one introduces the two dimensional Green's function defined by the solution of the following equation:

$$\begin{aligned} & \left(r^{-2} \partial / \partial r (r^2 \partial / \partial r) + V(r) + r^{-2} \hat{L}_\theta + i(2m\tau\gamma_r) \right) G(r, \theta | \rho, \theta_1; m) \\ & = (r^2 \sin \theta)^{-1} \delta(r - \rho) \delta(\theta - \theta_1), \end{aligned} \quad (3.3.2)$$

where the right-hand side is the δ -function expression in the spherical coordinates r and θ . By using this Green's function the solution of (3.3.1) can be written formally as follows:

$$\psi_1^{(2m)}(r, \theta) = \int_1^\infty \int_0^\pi G(r, \theta | \rho, \theta_1; m) (-im \sin^2 \theta_1) \rho^3 \{g_0^{1/2}(\rho)\}' \sin \theta_1 d\theta_1 d\rho \quad (3.3.3)$$

where the homogeneous solution doesn't appear, for the differential operator $\{r^{-2} \partial / \partial r (r^2 \partial / \partial r) + V(r) + r^{-2} \hat{L}_\theta\}$ is hermitian and $i(2m\tau\gamma_r)$ is purely imaginary, as mentioned in the section 2.2), and the radial variable ρ in the integral runs over the range $1 \leq r < \infty$ because of the particular ansatz for intermolecular potential (3.1.1). Now our task is to find the two dimensional Green's function $G(r, \theta | \rho, \theta_1; m)$ in (3.3.2). The left-hand side of the eq.(3.3.2) is separable, and

$$\hat{L}_\theta := \sin^{-1} \theta \partial / \partial \theta (\sin \theta \partial / \partial \theta) - 4m^2 / \sin^2 \theta \text{ defined in (2.2.13D)}$$

is just the Legendre differential operator whose eigenfunctions and the corresponding eigenvalues are the associate Legendre functions $P_1^{2m}(\cos \theta)$ and $-1(1 + 1)$, respectively. That the eigenfunctions $P_1^{2m}(\cos \theta)$ should be finite over the whole range of $\theta (0 \leq \theta \leq \pi)$, requires l to be an integer larger or equal to $|2m|$. The Green's function $G(r, \theta | \rho, \theta_1; m)$ may be expanded in its eigenfunctions of angular part as follows:

$$\begin{aligned} G(r, \theta | \rho, \theta_1; m) &= \sum_{l \geq |2m|}^\infty (r_1(r | \rho; m) (2l+1) (1-2m)! / \{2(1+2m)!\} \\ &\cdot P_1^{2m}(\cos \theta) P_1^{2m}(\cos \theta_1)), \end{aligned} \quad (3.3.4)$$

where the nondiagonal terms don't appear, since the Green's function is diagonalized by the eigenfunctions, and the normalization factor comes from the following orthogonality relation

$$\int_0^\pi P_1^{2m}(\cos\theta) P_1^{2m}(\cos\theta) \sin\theta \, d\theta = \{2(1+2m)!\} \{(2l+1)(1-2m)!\}^{-1} \delta_{11},.$$

The radial factor $\Gamma_1(r|\rho;m)$ in (3.3.4) is the one dimensional Green's function which satisfies the following equation obtained by substituting $G(r,\theta|\rho,\theta_1;m)$ from (3.3.4) into (3.3.2):

$$(\hat{B} + V(r)) \Gamma_1(r|\rho;m) = r^{-2} \delta(r-\rho), \quad (3.3.5)$$

$$\text{where } \hat{B} := \partial^2/\partial r^2 + 2r^{-1}\partial/\partial r + k_s^2 - 1(1+1)r^{-2}$$

is the spherical Bessel differential operator, and

$$k_s := e^{is\pi/4} |2m\gamma_r|^{1/2}$$

$$s := \text{sign}(m\gamma_r).$$

Since $V(r)$ in (3.3.5) is quite a complicated function, it is desirable to consider this function as a perturbation and obtain an approximate solution through perturbation expansion. But the function $V(r)$ contains some singularity at $r=1$. So it is not appropriate to take it (including the singularity) as a perturbation. If one does it, nevertheless, one meets a severe difficulty with the boundary condition (BC) for $\Gamma_1(r|\rho;m)$ at $r=1$. (Since the BC for G at $r=1$, (2.2.17B), contains the singular effect of the mean force w' , the BC of the one dimensional Green's function $\Gamma_1(r|\rho;m)$ and so that of the unperturbed solution $\Gamma_1^0(r|\rho;m)$ at $r=1$, (3.3.8B), should also contain it. If the whole part of $V(r)$ including the singularity is considered

as a perturbation, the unperturbed solution $\Gamma_1^0(r|\rho;m)$ of eq. (3.3.5), which is obtained by neglecting $V(=0)$, won't contain the singular effect of the mean force w' . But this result is not consistent with the BC at $r=1$.) Fortunately the singularity of the function $V(r)$ at $r=1$ may be cancelled out with the singular effect of the differential operator $\hat{B}$ at $r=1$ in (3.3.5), where use is to be made of the boundary condition for $\Gamma_1(r|\rho;m)$ at $r=1$, which is to be derived from the BC for G (2.2.17B) at $r=1$ and is similar to it:

$$\begin{aligned} (\{\hat{B}+V(r)\}\Gamma_1(r|\rho;m))_{r=1} &= \{(-V(r)+k_s^2-1(1+1)r^{-2}+V(r))\Gamma_1(r|\rho;m)\}_{r=1} \\ &= \{k_s^2 - 1(1+1)\}\Gamma_1(r|\rho;m)_{r=1}. \end{aligned}$$

Thus the equation (3.3.5) may be rewritten in the following way:

$$\{\hat{B}+V(r)\}\Gamma_1(r|\rho;m) = \{\hat{B}_0+V_0(r)\}\Gamma_1(r|\rho;m) = r^{-2}\delta(r-\rho), \quad (3.3.5)'$$

$$\text{where} \quad \hat{B}_0 := \begin{cases} \hat{B} + V, & \text{if } r=1, \\ \hat{B}, & \text{if } r>1, \end{cases}$$

$$V_0(r) := \begin{cases} 0, & \text{if } r=1, \\ V(r), & \text{if } r>1. \end{cases}$$

The new function $V_0(r)$ defined above contains no singularity and is small in the whole range of definition ($r \geq 1$), and so may be taken suitably as a perturbation to solve the equation (3.3.5)'. The equation for the unperturbed Green's function $\Gamma_1^0(r|\rho;m)$ is

$$\hat{B}_0 \Gamma_1^0(r|\rho;m) = r^{-2}\delta(r-\rho), \quad (3.3.6)$$

where the superscript "0" means "unperturbed with respect to the function $V_0(r)$ ". Then one can write the linear inhomogeneous integral equation for $\Gamma_1(r|\rho;m)$ introducing $\Gamma_1^0(r|\rho;m)$ as

follows /ECO/:

$$\Gamma_1(r|\rho;m) = \Gamma_1^0(r|\rho;m) - \int_{1+}^{\infty} \Gamma_1^0(r|r_1;m) V_0(r_1) \Gamma_1(r_1|\rho;m) r_1^2 dr_1, \quad (3.3.7)$$

which can be solved by iteration in the following way:

$$\Gamma_1^1(r|\rho;m) = \Gamma_1^0(r|\rho;m) - \int_{1+}^{\infty} \Gamma_1^0(r|r_1;m) V_0(r_1) \Gamma_1^0(r_1|\rho;m) r_1^2 dr_1$$

$$\Gamma_1^2(r|\rho;m) = \Gamma_1^0(r|\rho;m) - \int_{1+}^{\infty} \Gamma_1^0(r|r_1;m) V_0(r_1) \Gamma_1^1(r_1|\rho;m) r_1^2 dr_1$$

.....

and so on, (3.3.7)'

where the superscripts "0,1,2,..." denote "the zeroth-, the first-, the second-, ... order perturbation", respectively, and the point $r_1=1$ is missing for $V_0(1)=0$.

The starting point of the iterative solutions is the unperturbed solution $\Gamma_1^0(r|\rho;m)$ of (3.3.6), which satisfies the similar boundary conditions (BC's) to (2.2.17A,B) at $r=\infty$ and 1:

$$\lim_{r \rightarrow \infty} \{ (2T_*)^{-1} w'(r) \Gamma_1^0 + \partial/\partial r \Gamma_1^0 \} = 0 \quad (3.3.8A)$$

$$g_0 \partial/\partial r (\Gamma_1^0 / g_0^{1/2})$$

$$= g_0^{1/2} \{ (2T_*)^{-1} w'(r) \Gamma_1^0 + \partial/\partial r \Gamma_1^0 \} = 0 \text{ at } r=1. \quad (3.3.8B)$$

These BC's are sufficient for those for Γ_1 and so for the 2-dimensional Green's function stated in (2.2.17A,B), which can be checked by substituting (3.3.7) into the corresponding BC.

The unperturbed 1-dimensional Green's function $\Gamma_1^0(r|\rho;m)$ can be represented in terms of $A_1(r;m)$ and $B_1(r;m)$, the two different solutions of the following homogeneous differential equations corresponding to (3.3.6):

$$\hat{B}_0 A_1(r;m) = 0 \quad (3.3.9A)$$

$$\hat{B}_0 B_1(r;m) = 0 \quad (3.3.9B)$$

where $A_1(r;m)$ and $B_1(r;m)$ are discriminated from each other by the BC's similar to (3.3.8A,B) at $r=\infty$ and 1 respectively, as follows

$$\lim_{r \rightarrow \infty} \{ (2T_*)^{-1} w'(r) A_1 + d/dr A_1 \} = 0 \quad (3.3.10A)$$

$$g_0 d/dr (B_1 / g_0^{1/2})$$

$$= g_0^{1/2} \{ (2T_*)^{-1} w'(r) B_1 + d/dr B_1 \} = 0 \text{ at } r=1. \quad (3.3.10B)$$

It hasn't been required that each of A_1 and B_1 should satisfy the BC's at both ends, i.e. $r=1$ and ∞ , or they would be trivial ones. Now the solution of (3.3.6), $\Gamma_1^0(r|\rho;m)$ may be written as /MOR/:

$$\Gamma_1^0(r|\rho;m) = \begin{cases} W_{s,1}^{-1} \cdot B_1(r;m) A_1(\rho,m), & \text{if } 1 \leq r \leq \rho, \\ W_{s,1}^{-1} \cdot A_1(r;m) B_1(\rho,m), & \text{if } 1 \leq \rho \leq r, \end{cases} \quad (3.3.11)$$

where

$$W_{s,1} / \rho^2 := \Delta(B_1, A_1; \rho)$$

$$:= \{ B_1(r;m) d/dr A_1(r;m) - A_1(r;m) d/dr B_1(r;m) \}_{r=\rho}$$

is the Wronskian of the two functions at $r=\rho$ and $s := \text{sign}(m\tau_r)$, as defined in (3.3.5). The solution (3.3.11) satisfies the BC's (3.3.8A,B) both at $r=\infty$ and 1 automatically, if the first derivative of $\Gamma_1^0(r|\rho;m)$ at $r=\rho$ is defined by

$$\partial / \partial r \Gamma_1^0(r|\rho;m) = \{ \rho^2 \Delta(B_1, A_1; \rho) \}^{-1} A_1(\rho;m) d/dr B_1(r;m) \text{ for } r=\rho.$$

Since the operator $\hat{B}_0$ for $r=1$ in (3.3.5)' is different from that for $r>1$ by V , the 1-diminsional Green's function $\Gamma_1^0(r|\rho;m)$

or the two functions A_1 and B_1 should be calculated separately for the two different cases: a) $r>1$ and b) $r=1$.

a) Calculation of the unperturbed 1-dim. Green's function
outside the hard sphere ($r>1$):

The solution A_1 of the spherical Bessel equation (3.3.9A) can be immediately determined by the corresponding BC, (3.3.10A), as follows:

$$A_1(r;m) = h_1^{((3-s)/2)}(k_s r) \quad (3.3.12A)$$

The general solution of the spherical Bessel equation (3.3.9B) is

$$B_1(r;m) = h_1^{(1)}(k_s r) + c_{s,1} h_1^{(2)}(k_s r). \quad (3.3.12B)$$

The r.h.s. of (3.3.12A and B) are the spherical Hankel functions of first (if $s=1$) or second (if $s=-1$) kind, and their linear combination, respectively. The proportional constant in each solution of (3.3.12A,B) is not needed, since it is canceled in (3.3.11).

The coefficient $c_{s,1}$ cannot be determined by the BC for B_1 , (3.3.10B), since the solution (3.3.12B) is restricted to the region $r>1$: the boundary $r=1$ is excluded in (3.3.12B) and the solution of (3.3.9B) at $r=1$ is different in its functional form from that at $r>1$ given by (3.3.12B).

We now should find a new condition to determine the coefficient $c_{s,1}$ in (3.3.12B). To this end a deeper examination of the excess probability current density j_{12} , introduced in (2.2.14), near the boundary $r=1$ is needed. The radial component of $j_{12} =: j$ in (2.2.14),

$$j_r := (j_{12})_{\text{radial}}$$

may be rewritten as follows

$$\begin{aligned} j_r &= -\tau^{-1} g_0 \partial (g_0^{-1/2} \psi) / \partial r \\ &= \sum_{n=1}^{\infty} \sum_{m=-\infty}^{\infty} ((\tau \gamma_d)^n e^{i2m\phi} (j_r)_{n,2m}) \\ (j_r)_{n,2m} &:= -\tau^{-1} g_0 \partial \{g_0^{-1/2} \psi_n^{(2m)}(r, \theta)\} / \partial r, \end{aligned}$$

where use has been made of the expansions (2.2.9 and 11) and the component $(j_r)_{0,2m}$ doesn't appear, since $\psi_0^{(2m)} = 0$ for all m . The boundary condition (2.2.15B) for j_r at $r=1$ was $j_r=0$ or equivalently $(j_r)_{n,2m} = 0$ at $r=1$ for arbitrary values of γ_d . Since $g_0(r)$ is discontinuous at $r=1$ and its derivative is singular at $r=1$, this boundary condition at $r=1$ implies neither $j_r=0$ nor $(j_r)_{n,2m} = 0$ at $r=1^+$, as can be seen in the above expression. We should find some proper physical assumption in order to derive the condition for j_r at $r=1^+$. What kind of condition for j_r can be given at $r=1^+$?

Now the radial component of the excess probability current density, j_r , may be decomposed into the hard core and the soft force contribution in the following way:

$$\begin{aligned} j_r &= j_r^H + j_r^S \\ j_r^{H,S}(r, \theta, \phi) &= \sum_{n=1}^{\infty} \sum_{m=-\infty}^{\infty} ((\tau \gamma_d)^n e^{i2m\phi} (j_r^{H,S}(r, \theta))_{n,2m}) \\ (j_r^H(r, \theta))_{n,2m} &:= -\tau^{-1} g_0(r) \int_1^{1+} \int_0^\pi \partial \{G(r, \theta | r_1, \theta_1; m) / g_0^{1/2}(r)\} / \partial r \\ &\quad \cdot R_n^m(r_1, \theta_1) \sin \theta_1 d\theta_1 dr_1 \\ (j_r^S(r, \theta))_{n,2m} &:= -\tau^{-1} g_0(r) \int_1^\infty \int_0^\pi \partial \{G(r, \theta | r_1, \theta_1; m) / g_0^{1/2}(r)\} / \partial r \\ &\quad \cdot R_n^m(r_1, \theta_1) \sin \theta_1 d\theta_1 dr_1, \end{aligned} \tag{3.3.13}$$

where

$$R_1^m(r, \theta) := (\delta_{m,1} - \delta_{m,-1}) (-i \sin^2 \theta) r (g_0^{1/2}(r)) ,$$

$$R_n^m(r, \theta) := i(m-1-\hat{N}) \psi_n^{(2m-2)}(r, \theta) + i(m+1+\hat{N}) \psi_n^{(2m+2)}$$

for $n \geq 2$,

which are the inhomogeneous terms in the differential equations for the 2-dim. perturbation functions $\psi_n^{(2m)}$ (2.2.18A and B). In (3.3.13) the corresponding 2-dim. Green's function, G , defined by the equation (3.3.2), has been used.

The radial component of excess probability current density represented in terms of the Green's function G in (3.3.13) may be interpreted as the sum of the flowing effect due to the source (inhomogeneous term) R_n^m at (r_1, θ_1) on the flow of molecules at (r, θ) , where the relation between the source and the flowing effect is given by the Green's function. The source term $R_n^m(r_1, \theta_1)$ contains the effect of the mean force at (r_1, θ_1) , as can be seen in its definition in (3.3.13). This mean force has singularity at $r_1=1$. But, as one can see in (3.3.13), the soft force contribution j_r^S in (3.3.13) does not contain the singular effect of the source term. We will see later in b) that the Green's function G is proportional to $g_0^{1/2}(r)$ at $r=1$, and so no singularity arise from the both integrals in (3.3.13). Thus not only the sum of j_r^H and j_r^S but also each of them vanishes at $r=1$ separately, since each of them is in proportion to $g_0(r)$ which is zero at $r=1$, as shown in (3.3.13). We now assume that the soft force contribution to the radial component of the excess probability current density goes to zero continuously as $r \rightarrow 1$. In other words the soft force contribution to the radial component of the excess probability current density should vanish in the very vicinity of the hard core in the relative pair space:

$$\lim_{r \rightarrow 1+} j_r^S(r, \theta, \phi) = 0. \quad (3.3.13A)$$

The condition (3.3.13A) is based on the assumption of continuity of j_r^S for $r \geq 1$. We call it "the secondary boundary condition at $r=1^+$ ", since it is related to the boundary condition of j_r at $r=1$. It is noted that j_r^H need not be continuous at $r=1$ and so j_r need not, too.

The secondary boundary condition (3.3.13A) is equivalent to

$$\lim_{r \rightarrow 1^+} (j_r^S(r, \theta, \phi))_{n, 2m} = 0$$

for all the allowed integers m and n , as may be inferred from (3.3.13). On substituting the expansion of $G(r, \theta | r_1, \theta_1)$ (3.3.4) into the last expression for $(j_r^S)_{n, 2m}$ of (3.3.13), the above refined secondary boundary condition at $r=1^+$ may be rewritten more explicitly as follows

$$\begin{aligned} \lim_{r \rightarrow 1^+} (j_r^S(r, \theta))_{n, 2m} &= -\tau \lim_{r \rightarrow 1^+} g_0(r) \sum_{1 \leq |2m|}^{\infty} \{ (2l+1)(l-2m)! \\ &\quad \cdot \{ 2(1+2m)! \}^{-1} P_1^{2m}(\cos \theta) \int_{1^+}^{\infty} \partial / \partial r \{ \Gamma_1(r | r_1; m) / g_0^{1/2}(r) \} \\ &\quad \cdot \int_0^{\pi} P_1^{2m}(\cos \theta_1) R_n^m(r_1, \theta_1) \sin \theta_1 d\theta_1 dr_1 \} \\ &= 0. \end{aligned}$$

Since for $1^+ = r < r_1$

$$\begin{aligned} \Gamma_1(r | r_1; m) &= W_{s,1}^{-1} B_1(r; m) \{ A_1(r_1; m) \\ &\quad - \int_{1^+}^{\infty} A_1(r_2; m) V_0(r_2) \Gamma_1(r_2 | r_1; m) r_2^2 dr_2 \} \end{aligned}$$

from (3.3.7) and (3.3.11), the above condition may be written as

$$\lim_{r \rightarrow 1^+} g_0(r) d/dr \{ B_1(r; m) / g_0^{1/2}(r) \} = 0. \quad (3.3.13A)'$$

This is the secondary boundary condition at $r=1^+$ written in terms of the function $B_1(r; m)$. Here the following condition

$$\int_{1+}^{\infty} R_n^m(r_1, \theta_1) \{A_1(r_1; m) - \int_{1+}^{\infty} A_1(r_2; m) V_0(r_2) r_1(r_2 | r_1; m) r_2^2 dr_2\} dr_1 \neq 0$$

is assumed, which is somewhat evident. Otherwise, from the both equations stated above Eq.(3.3.13A)' the n-th derivative $(\partial/\partial r)^n \{j_r^S(r, \theta)\} = 0$ at $r = 1^+$ for all $n \geq 0$, which could be satisfied only in an unnatural way.

By making use of the secondary boundary condition at $r=1^+$ (3.3.13A)', the coefficient $c_{s,1}$ in (3.3.12B) may be determined. Substituting the solution for B_1 (3.3.12B) into (3.3.13A)' leads to

$$(2T_*)^{-1} w'(1^+) \{h_1^{(1)}(k_s) + c_{s,1} h_1^{(2)}(k_s r)\} + \{d/dr(h_1^{(1)}(k_s r) + c_{s,1} h_1^{(2)}(k_s r))\}_{r=1^+} = 0$$

or

$$c_{s,1} = -c_{s,1}^{(1)}/c_{s,1}^{(2)} \quad \text{with}$$

$$c_{s,1}^{(1)} = (2T_*)^{-1} w'(1^+) h_1^{(1)}(k_s) + \{d/dr h_1^{(1)}(k_s r)\}_{r=1^+}$$

$$c_{s,1}^{(2)} = (2T_*)^{-1} w'(1^+) h_1^{(2)}(k_s) + \{d/dr h_1^{(2)}(k_s r)\}_{r=1^+}, \quad (3.3.13B)$$

where

$$w'(1^+) = \lim_{r \rightarrow 1^+} dw(r)/dr = -T_* \lim_{r \rightarrow 1^+} g'_0(r)/g_0(r).$$

b) Calculation of the unperturbed 1-dim. Green's function at the hard sphere ($r=1$)

Since the pair-correlation function $g_0(r)$ vanishes discontinuously at $r=1$, the quantities such as $g_0(1)/g_0(1) = 0/0$,

$g'_0(1) - g'_0(1) = \infty - \infty$, etc. are not well defined. So $g_0(r)$ at $r=1$ is considered in the sense of definition as a limit of such a function $g_0(r; \lambda)$ with parameter λ :

$$g_0(r) = \lim_{\lambda \rightarrow \infty} g_0(r; \lambda),$$

and such indefinite quantities are understood in the following way:

$$g_0(1)/g_0(1) := \lim_{\lambda \rightarrow \infty} g_0(1; \lambda)/g_0(1; \lambda) = 1$$

$$g'_0(1) - g'_0(1) := \lim_{\lambda \rightarrow \infty} \{g'_0(1; \lambda) - g'_0(1; \lambda)\} = 0,$$

where $g_0(1; \lambda)$ is assumed to become infinitesimally small for large λ but nonzero, and $g'_0(1; \lambda)$ to become large for large λ but finite. The r -dependence of the functions at $r=1$, although they are zero or infinite at $r=1$, will be shown in order to perform algebra between them, as mentioned above.

One particular solution at $r=1$ of the homogeneous equation (3.3.9A or B) may be found to be $g_0^{1/2}(r)$. Another independent solution at $r=1$ is easily determined/MOR/ as

$$g_0^{1/2}(r) \int_1^r \rho^{-2} g_0^{-1}(\rho) d\rho.$$

Since the function B_1 should satisfy the BC at $r=1$ (3.3.10B), it is to be proportional to $g_0^{1/2}(r)$ at $r=1$. The function A_1 may be expressed in general as a linear combination of the two independent solutions, where it is noticed that the solution for A_1 at $r=1$ need not and cannot satisfy the BC at $r=\infty$ (3.3.10A).

Thus one has the following appropriate solutions for A_1 and B_1 at $r=1$:

$$A_1(r;m) = \alpha_1^{s,1} g_0^{1/2}(r) + \alpha_2^{s,1} g_0^{1/2}(r) \int_1^r \rho^{-2} g_0^{-1}(\rho) d\rho \quad (3.3.14A)$$

$$B_1(r;m) = \beta_1^{s,1} g_0^{1/2}(r) \quad \text{at } r=1. \quad (3.3.14B)$$

The constants $\alpha_1^{s,1}$, $\alpha_2^{s,1}$, and $\beta_1^{s,1}$ are determined in the following way.

On the one hand, one represents or defines the first derivative of B_1 at $r=1$ in terms of delta-function: Since $g_0^{1/2}(r)=0$ at $r=1$ and $g_0^{1/2} = g_0^{1/2}(1^+) \neq 0$ at $r=1^+$, one has from (3.3.14B)

$$\begin{aligned} B_1'(r;m) &= \beta_1^{s,1} \{g_0^{1/2}(r)\}' \\ &= \beta_1^{s,1} g_0^{1/2}(1^+) \delta(r-1) \quad \text{at } r=1. \end{aligned} \quad (3.3.14C)$$

The first derivative of A_1 in (3.3.14A)

$$\begin{aligned} A_1'(r;m) &= \alpha_1^{s,1} \{g_0^{1/2}(r)\}' + \alpha_2^{s,1} \{g_0^{1/2}(r)\}' \int_1^r \rho^{-2} g_0^{-1}(\rho) d\rho \\ &\quad + \alpha_2^{s,1} r^{-2} g_0^{-1/2}(r) \end{aligned}$$

cannot be well defined in terms of delta-function because of the term $g_0^{-1/2}(r)$. We examine rather the delta-function representation of the first derivative of $g_0^n(r)A_1(r;m)$ at $r=1$ for $n > 1/2$. On multiplying (3.3.14A) by $g_0^n(r)$ ($n > 1/2$) and taking the first derivative, one obtains

$$\begin{aligned} \{g_0^n(r)A_1(r;m)\}' &= \alpha_1^{s,1} \{g_0^{n+1/2}(r)\}' + \alpha_2^{s,1} \{g_0^{n+1/2}(r)\}' \int_1^r \rho^{-2} g_0^{-1}(\rho) d\rho \\ &\quad + \alpha_2^{s,1} r^{-2} g_0^{n-1/2}(r) \\ &= \alpha_1^{s,1} g_0^{n+1/2}(1^+) \delta(r-1) \quad \text{at } r=1, \end{aligned} \quad (3.3.14D)$$

where use has been made of the fact that $g_0^{n-1/2}(1)=0$ for $n>1/2$, and $\{g_0^{n+1/2}(r)\}' = g_0^{n+1/2}(1^+) \delta(r-1)$ at $r=1$, since $g_0^{n+1/2}=0$ at $r=1$ and $g_0^{n+1/2}=g_0^{n+1/2}(1^+) \neq 0$ at $r=1^+$ for $n>1/2$. The value of

the integral $\int_1^r \rho^{-2} g_0^{-1}(\rho) d\rho$ at $r=1$ is independent of the "hidden" parameter λ introduced in the beginning of this paragraph and so is identically zero at $r=1$.

On the other hand, since the functions $g_0^n A_1$ and B_1 jump from their zero values at $r=1$ to their nonzero values at $r=1^+$, their first derivatives at $r=1$ may be written in terms of delta-function as follows

$$\{g_0^n(r) A_1(r;m)\}' = g_0^n(1^+) A_1(1^+;m) \delta(r-1)$$

$$B_1'(r;m) = B_1(1^+;m) \delta(r-1) \quad \text{at } r=1. \quad (3.3.14E)$$

By comparing Eqs.(3.3.14C and D) with Eq.(3.3.14E) one may determine the values of $\alpha_1^{s,1}$ and $\beta_1^{s,1}$:

$$\begin{aligned} \alpha_1^{s,1} &= A_1(1^+;m)/g_0^{1/2}(1^+) = h_1^{(3-s)/2}(k_s)/g_0^{1/2}(1^+) \\ \beta_1^{s,1} &= B_1(1^+;m)/g_0^{1/2}(1^+) = \{h_1^{(1)}(k_s) + C_{s,1} h_1^{(2)}(k_s)\}/g_0^{1/2}(1^+), \end{aligned} \quad (3.3.14F)$$

where the values of A_1 and B_1 at $r=1^+$ are substituted from Eqs.(3.3.12A,B).

The remaining constant $\alpha_2^{s,1}$ can be determined in such a way that the Wronskian of A_1 and B_1 at $r=1$ may have the same value as that at $r=1^+$:

$$\Delta(B_1, A_1; 1) = \Delta(B_1, A_1; 1^+)$$

or

$$\beta_1^{s,1} \alpha_2^{s,1} = w_{s,1}$$

or

$$\alpha_2^{s,1} = w_{s,1} / \beta_1^{s,1}, \quad (3.3.14G)$$

where $W_{s,1}$ is defined in Eq.(3.3.11) and may now be calculated by using Eqs.(3.3.12A and B) as follows

$$\begin{aligned} W_{s,1} &= r^{2\Delta(B_1, A_1; r)} \\ &= (-2i/k_s) C_{s,1}^{((3-s)/2)} / C_{s,1}^{(2)}. \end{aligned} \quad (3.3.14H)$$

The function $V_0(r)$ is related to the long-range behavior of the equilibrium correlation function. Since the inhomogeneous term in the equation for $\Psi_1^{(2m)}(r, \theta)$ (3.3.1) contains the effect of the long-range behaviour of g_0 and one can see how this term affects $\Psi_1^{(2m)}(r, \theta)$ in the integral representation (3.3.3), one does not lose the first-order effect of the long-range behavior of g_0 on $\Psi_1^{(2m)}(r, \theta)$, if one uses the unperturbed Green's function given by (3.3.11) in the integral (3.3.3). More generally speaking, one obtains the effect of the long-range behavior of g_0 on $\Psi_1^{(2m)}(r, \theta)$ to the $(n+1)$ -th order, if one employs the n -th order approximation of one dimensional Green's function Γ_1^n from (3.3.7)' in the integral (3.3.3). In this section the unperturbed Green's function Γ_1^n only will be considered to avoid the mathematical complication, which still preserves the first-order effect of the long-range behavior of g_0 .

The unperturbed two dimensional Green's function is obtained by replacing Γ_1 in (3.3.4) by Γ_1^0 from (3.3.11) as follows

$$\begin{aligned} G^0(r, \theta | \rho, \theta_1; m) &= \sum_{l \geq |2m|}^{\infty} \Gamma_1^0(r | \rho; m) (2l+1) (1-2m)! \{2(1+2m)!\}^{-1} \\ &\quad \cdot P_1^{2m}(\cos \theta) P_1^{2m}(\cos \theta_1). \end{aligned} \quad (3.3.15)$$

This can be substituted again in (3.3.3) to obtain the following expression for the zeroth-order approximation for the deviation factor with respect to the perturbation $V_0(r)$:

$$\begin{aligned}
 {}^0\Psi_1^{(2m)}(r, \theta) &= \int_1^\infty \int_0^\pi G^0(r, \theta | \rho, \theta_1; m) (-i m \sin^2 \theta_1) \rho^3 (g_0^{1/2}(\rho))' \cdot \\
 &\quad \cdot \sin \theta_1 d\theta_1 d\rho \\
 &= \sum_{1 \geq |2m|} \left\{ (-i m) P_1^{2m}(\cos \theta) \int_1^\infty r_1^0(r | \rho; m) (g_0^{1/2}(\rho))' \rho^3 d\rho \right. \\
 &\quad \cdot (2l+1)(l-2m)! \{2(l+2m)!\}^{-1} \int_0^\pi P_1^{2m}(\cos \theta_1) \sin^3 \theta_1 d\theta_1 \Big\}.
 \end{aligned}$$

Since

$$\begin{aligned}
 &(2l+1)(l-2m)! \{2(l+2m)!\}^{-1} \int_0^\pi P_1^{2m}(\cos \theta_1) \sin^3 \theta_1 d\theta_1 \\
 &= \delta_{1,2} (\delta_{m,1}/3 + 8\delta_{m,-1}), \quad (3.3.16)
 \end{aligned}$$

the above expression for ${}^0\Psi_1^{(2m)}(r, \theta)$ may be enormously simplified as follows:

$$\begin{aligned}
 {}^0\Psi_1^{(2m)}(r, \theta) &= (-i m) P_1^{2m}(\cos \theta) (\delta_{m,1}/3 + 8\delta_{m,-1}) \\
 &\quad \cdot \int_1^\infty r_1^0(r | \rho; m) (g_0^{1/2}(\rho))' \rho^3 d\rho \\
 &= (-i m/3) (\delta_{m,1} + \delta_{m,-1}) P_2^2(\cos \theta) \int_1^\infty r_1^0(r | \rho; m) (g_0^{1/2}(\rho))' \rho^3 d\rho
 \end{aligned}$$

Substituting (3.3.11) for $r_1^0(r | \rho; m)$ into the above equation leads to

$$\begin{aligned}
 {}^0\Psi_1^{(2m)}(r, \theta) &= (-i m/3) (\delta_{m,1} + \delta_{m,-1}) P_2^2(\cos \theta) W_{s,2}^{-1} \\
 &\quad \cdot \{ \Lambda_2(r; m) \int_1^\infty B_2(\rho; m) \rho^3 (g_0^{1/2}(\rho))' d\rho \\
 &\quad + B_2(r; m) \int_1^\infty \Lambda_2(\rho; m) \rho^3 (g_0^{1/2}(\rho))' d\rho \}, \quad (3.3.17)
 \end{aligned}$$

where $W_{s,2}$ is defined in (3.3.11), and the relation

$$P_1^{-m}(x) = (-1)^m (1-m)! \{(1+m)!\}^{-1} P_1^m(x) \quad \text{for integers } m, l \quad (1 \geq |m|)$$

has been used. Since $\gamma_r = \gamma/2$ from (2.2.5), one has from the definition in (3.3.5)

$$s = \text{sign}(m\tau\gamma_r) = m \text{sign}(\gamma) \quad \text{for } m = \pm 1,$$

where $\tau = \sigma^2/D > 0$, since the diffusion constant D is always positive. From now on one assumes the positivity of the value of shear rate γ , and has the following relation of signs

$$s = m \quad \text{for } m = \pm 1. \quad (3.3.18)$$

On making use of (3.3.18) and substituting (3.3.17) into the reduced expression for ψ_1 , (2.2.19), one obtains finally the following solution for ψ_1 in the zeroth-order approximation with respect to the perturbation $V_0(r)$, but without losing the effect of the long-range behavior of g_0 , as mentioned before:

$$\begin{aligned} \psi_1^0(r, \theta, \phi) &= \sum_{m=\pm 1} {}^0\psi_1^{(2m)}(r, \theta) e^{i2m\phi} \\ &= (i/3) P_2^2(\cos\theta) \sum_{s=\pm 1} e^{i2s\phi} (-s/w_{s,2}) \cdot \\ &\quad \cdot (A_2(r;s) \int_1^r B_2(\rho;s) \rho^3 (g_0^{1/2}(\rho))' d\rho + \\ &\quad + B_2(r;s) \int_r^\infty A_2(\rho;s) \rho^3 (g_0^{1/2}(\rho))' d\rho). \end{aligned} \quad (3.3.19)$$

The function $(g_0^{1/2}(\rho))'$ contains the singular effect of the repulsive force at the effective hard core. Since the molecules do "see" the singular force, this effect should be taken into account. In a more natural way one can obtain this singular force effect, if one approximates the repulsive core of the effective potential $w(r)$ by a precipitous logarithmic wall, i.e. $w_{\text{core}}(r) = -\lambda \ln r$, and takes the limit $\lambda \rightarrow \infty$ after calculation, although this method includes much more mathematical complications than the hard-core approach. One can single out the singular effect from $(g_0^{1/2}(r))'$ in the similar way as before: since

$$g_0^{1/2}(r) = \begin{cases} 0, & \text{if } r=1 \\ g_0^{1/2}(1^+), & \text{if } r=1^+, \end{cases}$$

one obtains the following expression

$$(g_0^{1/2}(r))' = \begin{cases} g_0^{1/2}(1^+) \delta(r-1), & \text{if } r=1 \\ (g_0^{1/2}(r))', & \text{if } r>1, \end{cases}$$

and similarly

$$\begin{aligned} g_0'(r) &= \{(g_0^{1/2}(r))^2\}' = 2g_0^{1/2}(r) (g_0^{1/2}(r))' \\ &= \begin{cases} g_0(1^+) \delta(r-1), & \text{if } r=1 \\ g_0'(r), & \text{if } r>1. \end{cases} \end{aligned} \quad (3.3.20)$$

For the sake of simplicity of the formalism the following notations are introduced:

$$\int_Y^Z ((3-t)/2) (k_s) = \int_Y^Z h_2^{((3-t)/2)} (k_s r) r^3 (g_0^{1/2}(r))' dr \quad (3.3.21A)$$

$$\int_Y^Z J(k_s) = \int_Y^Z j_2^z(k_s r) r^3 (g_0^{1/2}(r))' dr \quad (3.3.21B)$$

$$\int_Y^Z N(k_s) = \int_Y^Z n_2^z(k_s r) r^3 (g_0^{1/2}(r))' dr \quad (3.3.21C)$$

where $s = \pm 1$, $t = \pm 1$; $y, z \geq 1$;

$$g_0(r) = g_0(1^+) \text{ for } r=1 \text{ and } g_0(r) \text{ for } r>1. \quad (3.3.21D)$$

It is noted that $g_0'(1) := g_0'(1^+)$ in the integrands of Eqs. (3.3.21A-C).

The deviation of nonequilibrium pair-correlation function from equilibrium is $g_0\chi$ and χ was defined by $\chi = g_0^{-1/2}\psi$ in (2.2.7). Thus the perturbation coefficient of χ corresponding to ψ_n^p may be written as

$$\chi_n^p := g_0^{-1/2}\psi_n^p, \quad (3.3.22)$$

where the sub- and the superscript, n and p , mean the orders of perturbations with respect to the deformation parameter and the perturbation function $V_0(r)$ in (3.3.5)', respectively. Substitution of (3.3.19) into (3.3.22) leads to

$$\begin{aligned} \chi_1^0 = & (i/3)P_2^2(\cos\theta) \sum_{s=\pm 1} e^{i2s\phi} (-s/W_{s,2}) \cdot \\ & \cdot (g_0^{-1/2}(r)A_2(r;s) \int_1^r B_2(\rho;s) \rho^3 (g_0^{1/2}(\rho))' d\rho + \\ & + g_0^{-1/2}(r)B_2(r;s) \int_r^\infty A_2(\rho;s) \rho^3 (g_0^{1/2}(\rho))' d\rho), \quad (3.3.19)' \end{aligned}$$

where the factor $g_0^{-1/2}(r)$ is combined with the terms in the angular bracket. This factor is singular at $r=1$. Thus the factor $g_0^{-1/2}(r)$ gives some finite contribution at $r=1$ when it is multiplied by a quantity proportional to $g_0^{1/2}(r)$, where the multiplication is to be understood in the sense of the limit of the "hidden" parameter, as already mentioned.

Since the functions A_2 , B_2 , and g_0 are discontinuous at $r=1$, the function χ_1^0 is to be calculated separately for the two different regions: $r=1$ and $r>1$. On substituting (3.3.14 A,B) for A_2 and B_2 at $r=1$, and on making use of (3.3.20) for the delta-function expression of $g_0'(r) = g_0(1^+) \delta(r-1)$, into the above representation for χ_1^0 , one obtains the following expressions for the two different regions:

for $r=1$

$$\begin{aligned}
 \chi_1^0 &= (i/3) P_2^2(\cos\theta) \sum_{s=\pm 1} e^{i2s\phi} (-s/W_{s,2}) \cdot \\
 &\cdot \{ \alpha_1^{s,1} \int_{\{1\}} \beta^{s,1} g_0^{1/2}(\rho) \rho^3 (g_0^{1/2}(\rho))' d\rho + \\
 &+ \beta_1^{s,1} \int_{\{1\}} \{ \alpha_1^{s,1} + \alpha_2^{s,1} \rho_1^{-2} g_0^{-1}(\tau) d\tau \} g_0^{1/2}(\rho) \rho^3 (g_0^{1/2}(\rho))' d\rho + \\
 &+ \beta_1^{s,1} \int_{1+}^{\infty} A_2(\rho;s) \rho^3 (g_0^{1/2}(\rho))' d\rho \} \\
 &= (i/3) P_2^2(\cos\theta) \sum_{s=\pm 1} e^{i2s\phi} (-s/W_{s,2}) \cdot \\
 &\cdot (2^{-1} \alpha_1^{s,1} \beta^{s,1} g_0(1^+) + 2^{-1} \beta^{s,1} \alpha_1^{s,1} g_0(1^+) + \\
 &\quad + \beta^{s,1} \int_{1+}^{\infty} A_2(\rho;s) \rho^3 (g_0^{1/2}(\rho))' d\rho) \\
 &= (i/3) P_2^2(\cos\theta) \sum_{s=\pm 1} e^{i2s\phi} (-s/W_{s,2}) \cdot \\
 &\cdot (\alpha_1^{s,1} \beta^{s,1} g_0(1^+) + \beta^{s,1} \int_{1+}^{\infty} A_2(\rho;s) \rho^3 (g_0^{1/2}(\rho))' d\rho)
 \end{aligned}
 \tag{3.3.19A}$$

and for $r>1$

$$\begin{aligned}
 \chi_1^0 &= (i/3) P_2^2(\cos\theta) \sum_{s=\pm 1} e^{i2s\phi} (-s/W_{s,2}) \cdot \\
 &\cdot (g_0^{-1/2}(r) A_2(r;s) \{ \int_{\{1\}} \beta^{s,1} g_0^{1/2}(\rho) \rho^3 (g_0^{1/2}(\rho))' d\rho + \\
 &\quad + \int_{1+}^r B_2(\rho;s) \rho^3 (g_0^{1/2}(\rho))' d\rho \} + \\
 &\quad + g_0^{-1/2}(r) B_2(r;s) \int_r^{\infty} A_2(\rho;s) \rho^3 (g_0^{1/2}(\rho))' d\rho) \\
 &= (i/3) P_2^2(\cos\theta) \sum_{s=\pm 1} e^{i2s\phi} (-s/W_{s,2}) g_0^{-1/2}(r) (2^{-1} \beta^{s,1} g_0(1^+) A_2(r;s) + \\
 &\quad + B_2(r;s) \int_{1+}^{\infty} A_2(\rho;s) \rho^3 (g_0^{1/2}(\rho))' d\rho + \\
 &\quad + A_2(r;s) \int_{1+}^r B_2(\rho;s) \rho^3 (g_0^{1/2}(\rho))' d\rho - \\
 &\quad - B_2(r;s) \int_{1+}^r A_2(\rho;s) \rho^3 (g_0^{1/2}(\rho))' d\rho),
 \end{aligned}
 \tag{3.3.19B}$$

where the relation $f_r^\infty = f_{1+}^\infty - f_{1+}^r$ for $r > 1$ has been used.

One substitutes (3.3.14F,H) for $\alpha_1^{s,1}$, $\beta^{s,1}$ and $w_{s,2}$, and (3.3.12A,B) for A_2 and B_2 , into (3.3.19A,B)', and makes use of the notation and definition (3.3.21A,D):

$$\begin{aligned} \chi_1^0(r, \theta, \phi) = & (i/3) P_2^2(\cos \theta) \sum_{s=\pm 1} e^{i2s\phi} \{ (-i/2) s k_s C_{s,2}^{(2)} / C_{s,2}^{((3-s)/2)} \} \cdot \\ & \cdot g_0^{-1/2}(r) \{ 2^{-1} (1 + \delta_{1,r}) g_0^{1/2}(1^+) \cdot \\ & \cdot \{ h_2^{(1)}(k_s) + C_{s,2} h_2^{(2)}(k_s) \} h_2^{((3-s)/2)}(k_s r) + \\ & + \{ h_2^{(1)}(k_s r) + C_{s,2} h_2^{(2)}(k_s r) \} H_1^\infty((3-s)/2)(k_s) + \\ & + \{ H_1^r(k_s) + C_{s,2} H_1^r(k_s) \} h_2^{((3-s)/2)}(k_s r) - \\ & - \{ h_2^{(1)}(k_s r) + C_{s,2} h_2^{(2)}(k_s r) \} H_1^r((3-s)/2)(k_s) \}. \end{aligned}$$

Since

$$\begin{aligned} & \{ C_{s,2}^{(2)} / C_{s,2}^{((3-s)/2)} \} \{ \{ H_1^r(k_s) + C_{s,2} H_1^r(k_s) \} h_2^{((3-s)/2)}(k_s r) - \\ & - \{ h_2^{(1)}(k_s r) + C_{s,2} h_2^{(2)}(k_s r) \} H_1^r((3-s)/2)(k_s) \} \\ = & h_2^{(2)}(k_s r) H_1^r(k_s) - h_2^{(1)}(k_s r) H_1^r(k_s), \end{aligned}$$

the above expression becomes

$$\begin{aligned} \chi_1^0(r, \theta, \phi) = & (1/6) P_2^2(\cos \theta) g_0^{-1/2}(r) \sum_{s=\pm 1} e^{i2s\phi} k_s \cdot \\ & \cdot \{ (s/2) (1 + \delta_{1,r}) g_0^{1/2}(1^+) \cdot \\ & \cdot \{ C_{s,2}^{(2)} h_2^{(1)}(k_s) - C_{s,2}^{(1)} h_2^{(2)}(k_s) \} h_2^{((3-s)/2)}(k_s r) / C_{s,2}^{((3-s)/2)} + \\ & + s \{ C_{s,2}^{(2)} h_2^{(1)}(k_s r) - C_{s,2}^{(1)} h_2^{(2)}(k_s r) \} H_1^\infty((3-s)/2)(k_s) / C_{s,2}^{((3-s)/2)} + \\ & + s h_2^{(2)}(k_s r) H_1^r(k_s) - s h_2^{(1)}(k_s r) H_1^r(k_s) \}, \end{aligned}$$

where the definition $C_{s,1} := -C_{s,1}^{(1)}/C_{s,1}^{(2)}$ from (3.3.13B) has been used.

This expression may be further simplified if one makes use of the following complex conjugate relations

$$\begin{aligned} k &:= k_+ = \bar{k}_- ; & h_2^{(1)}(k_+) &= \overline{h_2^{(2)}(k_-)} ; \\ C_+^{(1)} &:= C_{+1,2}^{(1)} = \overline{C_{-1,2}^{(2)}} =: \overline{C_-^{(2)}} \end{aligned} \quad (3.3.23)$$

and the result of the calculation:

$$\begin{aligned} C_+^{(1)} h_2^{(2)}(k) - C_+^{(2)} h_2^{(1)}(k) &= \left\{ (2T_*)^{-1} w'(1^+) h_2^{(1)}(k) + \right. \\ &\quad \left. + \{d/dr h_2^{(1)}(kr)\}_{r=1} \right\} h_2^{(2)}(k) - \\ &\quad - \left\{ (2T_*)^{-1} w'(1^+) h_2^{(2)}(k) + \{d/dr h_2^{(2)}(kr)\}_{r=1} \right\} h_2^{(1)}(k) \end{aligned}$$

from Def. (3.3.13B)

$$= -k\Delta(h_2^{(1)}, h_2^{(2)}; k) \quad \text{from the def. of Wronskian (3.3.11)}$$

$$= -k(-2i/k^2)$$

$$= 2i/k. \quad (3.3.24)$$

Thus one can write the expression for χ_1^0 as follows

$$\begin{aligned} \chi_1^0(r, \theta, \phi) &= (1/3) P_2^2(\cos \theta) \tilde{g}_0^{-1/2}(r) \operatorname{Re}(-e^{i2\phi} F(k, r)) \quad \text{with} \\ F(k, r) &= i(1+\delta_{1,r}) g_0^{1/2}(1^+) h_2^{(1)}(kr)/C_+^{(1)} + \\ &\quad + k \{C_+^{(1)} h_2^{(2)}(kr) - C_+^{(2)} h_2^{(1)}(kr)\} \frac{H_1^{(1)}(k)}{1} / C_+^{(1)} + \\ &\quad + k h_2^{(1)}(kr) \frac{H_1^{(2)}(k)}{1} - k h_2^{(2)}(kr) \frac{H_1^{(1)}(k)}{1}, \end{aligned} \quad (3.3.25A)$$

where k and $C_+^{(1)}$, and $\tilde{g}_0$ are defined by (3.3.23) and (3.3.21D), respectively.

The expression (3.3.25A) is pertaining to seeing the limiting behavior of χ_1^0 for large values of r or k . To see the limiting behavior of χ_1^0 for small k the following equivalent expression for χ_1^0 may be employed:

$$\begin{aligned} \chi_1^0(r, \theta, \phi) &= (1/3) P_2^2(\cos \theta) g_0^{-1/2}(r) \operatorname{Re} \{-e^{i2\phi} F(k, r)\} \quad \text{with} \\ F(k, r) &= i(1 + \delta_{1,r}) g_0^{1/2}(1^+) h_2^{(1)}(kr) / C_+^{(1)} + \\ &+ k \{ (C_+^{(1)} - C_+^{(2)}) j_2(kr) - i(C_+^{(1)} + C_+^{(2)}) n_2(kr) \} H_1^{(1)}(k) / C_+^{(1)} + \\ &+ 2ik n_2(kr) \frac{r}{1} J(k) - 2ik j_2(kr) \frac{r}{1} N(k), \end{aligned} \quad (3.3.25B)$$

where $C_+^{(1,2)}$, $J(k)$, $N(k)$, and g_0 are defined by (3.3.13, 21B, and 21D), respectively, and

$$\begin{aligned} C_+^{(1)} + C_+^{(2)} &= T_*^{-1} w'(1^+) j_2(k) + 2 \{ d/dr j_2(kr) \}_{r=1} \\ C_+^{(1)} - C_+^{(2)} &= i \{ T_*^{-1} w'(1^+) n_2(k) + 2 \{ d/dr n_2(kr) \}_{r=1} \}. \end{aligned}$$

The two alternative expressions (3.3.25A,B) are the general solutions for the deviation factor in the first-order perturbation theory and the deviation is given by $(\tau \gamma_d) g_0(r) \chi_1^0(r, \theta, \phi)$. The real property of correlation function has been fulfilled in a natural way. The effect of the long-range behavior of g_0 is concealed mainly in the integral $H_1^{(1)}(k)$, which is independent of r . It should be noticed that the deviation factor χ_1^0 contains the long-range effect of g_0 even for a small value of r because of the r -independent integral, i.e. the long-range behavior of correlation function in equilibrium affects both the short-range and the long-range behavior in nonequilibrium. The viscosity coefficient, which is mainly determined by the short-range behavior of nonequilibrium correlation function, is thus closely related to the long-range behavior of g_0 , and the delicate behaviors of viscosity coefficient (e.g., its functional

dependence on the correlation length) cannot be explained with such an oversimplified functional form of $g_0(r)$ for large r like that introduced by Kirkwood /KIR2/. The solution (3.3.25A or B) shows the correct functional dependence of the perturbation function χ_1^0 on $k(=k_+ = e^{i\pi/4}(2\tau\gamma_r)^{1/2})$ defined in (3.3.5, 23), which is a successful result of the perturbation expansion in the deformation parameter. Owing to this wide variety of functional dependence of χ_1^0 on k (or the shear rate) and the improved O-Z approximation for $g_0(r)$ one can see in the next chapter various interesting behaviors of the viscosity coefficients.

(ii) Solutions with the improved O-Z approximation of equilibrium density-density correlation function

In the expression (3.3.25A) all the terms are in their explicit forms except for the integrals of the form (3.3.21A)

$$\begin{aligned} \frac{r}{h_1}((3-t)/2)(k_s) &= \int_1^r h_2^{((3-t)/2)}(k_s \rho) \rho^3 \{g_0^{1/2}(\rho)\}' d\rho \\ &= \int_{1+}^r h_2^{((3-t)/2)}(k_s \rho) \rho^3 \{g_0^{1/2}(\rho)\}' d\rho \\ &\text{for } t = \underline{+1} \text{ and } s = \underline{+1}, \end{aligned}$$

which will be calculated by using the improved O-Z approximations for g_0 represented by (3.2.33). Since the spherical Hankel function of second order in the integrand is

$$h_2^{((3-t)/2)}(z_s) = i t \exp(it z_s) (z_s^{-1} + i 3 t z_s^{-2} - 3 z_s^{-3})$$

$$\text{with } z_s = k_s r,$$

the above integral may be rewritten as follows

$$\frac{r}{H}((3-t)/2)(k_s) = i t k_s^{-3} \int_{1+}^r e^{i t k_s \rho} (k_s^2 \rho^2 + i 3 t k_s \rho - 3) \{g_0^{1/2}(\rho)\}' d\rho. \quad (3.3.26)$$

The square root of $g_0(\rho)$ in (3.3.26) is not appropriate to the analytic execution of the integral and its approximate form may be introduced in the following way:

$$g_0^{1/2}(r) = \{1 + s^>(r)\}^{1/2} = 1 + s^>(r)/2 + \dots \\ \approx 1 + s^>(r)/2 \quad \text{for } r > 1, \quad (3.3.27)$$

which is reasonable for the range of large r , where $s^>(r)$ is very small, although $s^>(r)$ is not always small near the effective hard core. The improved O-Z approximations for $s^>(r)$ are given by (3.2.33).

By using (3.3.27) the integral (3.3.26) may be approximated as follows:

$$\frac{r}{H}((3-t)/2)(k_s) \approx \frac{r}{H^A}((3-t)/2)(k_s) \\ := i t k_s^{-3} \int_{1+}^r e^{i t k_s \rho} (k_s^2 \rho^2 + i 3 t k_s \rho - 3) \{s^>(\rho)/2\}' d\rho, \quad (3.3.28)$$

where the subscript "A" means the approximation for $g_0^{1/2}$, (3.3.27), and the constant term in (3.3.27) has vanished on taking the first derivative.

The approximated integral (3.3.28) can be calculated by replacing $s^>$ in the integrand by its improved O-Z approximation (3.2.33). Since

$$s^>_1(r) = \Sigma_1^\#(u_1/r) e^{v_1(r-1)} (v_1-1/r),$$

the approximated integral becomes

$$IOZ_{HA}^r((3-t)/2)(k_s)$$

$$= (it/2)k_s^{-3} \Sigma_1^{\#} u_1 e^{-v_1} \int_{1+}^r e^{(v_1+itk_s)\rho} (k_s^2 \rho^2 + i3tk_s \rho - 3)(v_1 - 1/\rho) / \rho d\rho,$$

where "#" may be replaced by the statement number of some improved O-Z approximation for $s^>(r)$, which can be chosen in the section 3.2), and the summation means the corresponding statement. After some calculation one obtains the following result for the integral above:

$$IOZ_{HA}^r((3-t)/2)(k_s)$$

$$\begin{aligned} = & (i/2)k_s^{-3} \Sigma_1^{\#} u_1 e^{-v_1} \{ e^{(v_1+itk_s)r} \{-3tr^{-1} + tv_1(3+v_1r) + \\ & + ik_s(1-v_1r) - tv_1^2(4+v_1r)(v_1+itk_s)^{-1} + tv_1^3(v_1+itk_s)^{-2}\} + \\ & + e^{(v_1+itk_s)} \{3t - tv_1(3+v_1) - ik_s(1-v_1) + \\ & + tv_1^2(4+v_1)(v_1+itk_s)^{-1} - tv_1^3(v_1+itk_s)^{-2}\} \}, \quad (3.3.29A) \end{aligned}$$

where "IOZ" means the improved O-Z approximation for $s(r)$. Especially, if $r \rightarrow \infty$ with the signs of $t = +1$ and $s = +1$, the first term in the angular bracket of (3.3.29A) vanishes, since

$$\text{Re}(ik_+r) = \text{Re}\{ie^{i\pi/4}(2\tau\gamma_r)^{1/2}r\} < 0, \quad \text{and}$$

one has the following r -independent approximated integral of the form

$$\begin{aligned} IOZ_{HA}^{\infty(1)}(k) = & (i/2)k^{-3} e^{ik} \Sigma_1^{\#} u_1 \{ 3 - v_1(3+v_1) - ik(1-v_1) + \\ & + v_1^2(4+v_1)(v_1+ik)^{-1} - v_1^3(v_1+ik)^{-2} \}, \quad (3.3.29B) \end{aligned}$$

where $k := k_+$.

If the expression for χ_1^0 of the second type (3.3.25B) is desired, one can make use of the following relations

$$\begin{aligned} \text{IOZ}_{JA}^r(k_s) &= 2^{-1} (\text{IOZ}_{HA}^{r(1)}(k_s) + \text{IOZ}_{HA}^{r(2)}(k_s)) \\ \text{IOZ}_{NA}^r(k_s) &= (2i)^{-1} (\text{IOZ}_{HA}^{r(1)}(k_s) - \text{IOZ}_{HA}^{r(2)}(k_s)), \end{aligned} \quad (3.3.29C)$$

which may be derived from the definitions (3.3.21A,B,C).

The last factor of the second term of $F(k,r)$ in each of (3.3.25A and B)

$$\frac{\infty}{1A} (k) / C_+^{(1)}$$

plays the most important role together with the first term in the viscosity problem, as will be seen in the next chapter. This factor converges at both $k=0$ and $|k|=\infty$, and is independent of r . For the later use it may be written here in its calculated form. From the definition for $C_+^{(1)}$ (3.3.13B) one has

$$\begin{aligned} \text{IOZ}_{HA}^{\infty(1)}(k) / C_+^{(1)} \\ = \text{IOZ}_{HA}^{\infty(1)}(k) / \left\{ (2T_*)^{-1} w'(1^+) h_2^{(1)}(k) + \{\partial/\partial r h_2^{(1)}(kr)\}_{r=1} \right\}, \end{aligned}$$

or, after some algebra, one obtains

$$B(k) := \text{IOZ}_{HA}^{\infty(1)}(k) / C_+^{(1)} = N(k) / Q(k), \quad (3.3.29D)$$

with

$$\begin{aligned} N(k) := \Sigma_1^{\#} u_1 \{ 3 - v_1(3+v_1) - ik(1-v_1) + \\ + v_1^2(4+v_1)(v_1+ik)^{-1} - v_1^3(v_1+ik)^{-2} \} \end{aligned}$$

$$Q(k) := Q_0 \{ 1 - ik + Q_2 k^2 + iQ_3 k^3 \}$$

$$Q_0 := 18 - 3T_*^{-1} w'(1^+); \quad Q_2 := \{ T_*^{-1} w'(1^+) - 8 \} / Q_0; \quad Q_3 := 2 / Q_0,$$

where u_1 's and v_1 's are given by the statement number replacing "#", e.g. $\# := (3.2.31)$ (the fourth-order approximation for $s_{PYH}^>(r)$). With (3.3.29A-D) showing the integrals performed by using the improved O-Z approximation of $s^>(r)$ and (3.3.27) one can write the deviation factor instead of (3.3.25A,B) as follows:

$$\begin{aligned} \text{IOZ}_{x_1}^0(r, \theta, \phi) &= (1/3)P_2^2(\cos\theta)g_0^{-1/2}(r) \operatorname{Re}\{-e^{i2\phi} \mathring{F}(k, r)\} \quad \text{with} \\ \mathring{F}(k, r) &= i(1+\delta_{1,r})(1+s_1^>/2)h_2^{(1)}(kr)/C_+^{(1)} + \\ &\quad + k\{C_+^{(1)}h_2^{(2)}(kr) - C_+^{(2)}h_2^{(1)}(kr)\}\text{IOZ}_{H_A}^{\infty(1)}(k)/C_+^{(1)} + \\ &\quad + kh_2^{(1)}(kr)\text{IOZ}_{H_A}^r(2)(k) - kh_2^{(2)}(kr)\text{IOZ}_{H_A}^r(1)(k), \quad (3.3.30A) \end{aligned}$$

or equivalently

$$\begin{aligned} \text{IOZ}_{x_1}^0(r, \theta, \phi) &= (1/3)P_2^2(\cos\theta)g_0^{-1/2}(r) \operatorname{Re}\{-e^{i2\phi} \mathring{F}(k, r)\} \quad \text{with} \\ \mathring{F}(k, r) &= i(1+\delta_{1,r})(1+s_1^>/2)h_2^{(1)}(kr)/C_+^{(1)} + \\ &\quad + k\{(C_+^{(1)} - C_+^{(2)})j_2(kr) - i(C_+^{(1)} + C_+^{(2)})n_2(kr)\}\text{IOZ}_{H_A}^{\infty(1)}(k)/C_+^{(1)} + \\ &\quad + 2ikn_2(kr)\text{IOZ}_{J_A}^r(k) - 2ikj_2(kr)\text{IOZ}_{N_A}^r(k), \quad (3.3.30B) \end{aligned}$$

where the superscript "IOZ" denotes the improved O-Z approximation of $s^>(r)$ and the subscript "A" means the approximation for $g_0^{1/2}$ (3.3.27). The function g_0 is defined by (3.3.21D). The factor $(1+s_1^>/2)$ with the definition

$$s_1^> := s^>(1^+) = g_0(1^+) - 1, \quad (3.3.30C)$$

is the approximation of the function $g_0^{1/2}(r)$ at $r = 1^+$, which is performed in (3.3.27). This approximation for $g_0^{1/2}(1^+)$ seems to be unreasonable, since $g_0(r)$ is no more small at $r=1^+$. The reason for the approximation is the following. The correct value of the factor $g_0^{1/2}(1)$ was singled out from the integrals

in (3.3.19) and written correctly in (3.3.25A,B), where the integrals also preserve the function $g_0^{1/2}(r)$ in its correct form in their integrands. But the function $g_0^{1/2}(r)$ in the integrals in (3.3.30A,B) is approximated by (3.3.27). Thus it is reasonable to take the factor $g_0^{1/2}(1^+)$, which is singled out, also in its approximated form written in (3.3.30A,B), for some cancelation of similar terms may occur between the singled-out and the integral terms. This possibility of cancelation could be seen more naturally if one had performed the approximation of the function $g_0^{1/2}(r)$ from the beginning in the integrals of the original representation given by (3.3.19), which was avoided to derive first the correct expressions (3.3.25A,B).

3.4) Limiting features of the first-order deviation factor χ_1^0

As the explicit solution for the deviation factor χ_1^0 (the first-order perturbation function) has been accomplished in the last section, it is interesting to examine its limiting features and inquire into their physical meanings. The following four situations with the variables r , k_s , and v_1 's are taken into account: (i) The r -dependence for large r , (ii) the shear-rate dependence for small shear rate with $|k| \ll |v_1| \neq 0$, (iii) the shear-rate dependence for small k with $1 > |k| \gg |v_1|$, and (iv) the shear-rate dependence for large shear rate, where v_1 's are related to the inverse correlation length which was discussed in the section 3.2), and r is assumed to be not so large in the cases (ii), (iii), and (iv). For each case the expressions for the deviation factor $^{IOZ}\chi_1^0$ (3.3.30A, B) will be used. The deviation itself is given by

$$(\text{deviation}) = g_0(r) \chi(r, \theta, \phi) \cong g_0(r) \left\{ (\tau \chi_0^0) ^{IOZ}\chi_1^0(r, \theta, \phi) \right\} \quad (3.4.0)$$

from the definitions (3.3.22) and (2.2.7), and the perturbation expansion (2.2.9).

(i) r -dependence of the deviation factor for large r (finite $k \neq 0$)

The expression (3.3.30A) is more pertinent to seeing this behavior than (3.3.30B). Since $g_0(r) \rightarrow 1$ as $r \rightarrow \infty$, it is sufficient to examine the function $\tilde{F}(k, r)$ in (3.3.30A), which can be rewritten as follows:

$$\begin{aligned} \tilde{F}(k, r) \equiv & k h_2^{(1)}(k, r) ^{IOZ} \tilde{H}_A^{(2)}(k) + k h_2^{(2)}(k, r) \left\{ ^{IOZ} \tilde{H}_A^{\infty(1)}(k) - ^{IOZ} \tilde{H}_A^{r(1)}(k) \right\} + \\ & + i(1 + \delta_{1,r})(1 + \frac{1}{2} \tilde{s}_1) \frac{1}{C_+^{(1)}} h_2^{(1)}(k, r) - k C_+^{(2)} h_2^{(1)}(k, r) B(k), \quad (3.4.1) \end{aligned}$$

where

$B(k)$ is defined in (3.3.29D).

The asymptotic representations of spherical Hankel functions of integer order can be easily seen from their closed form $[\bar{A}ER]$. Especially those of second order are shown just above (3.3.26) and their asymptotic form for large r are:

$$h_2^{(\frac{3-t}{2})}(k r) \sim \frac{i t}{k r} e^{i t k r} \quad \text{for } t = \pm 1. \quad (3.4.2)$$

On using the results (3.3.29A, B) and (3.4.2), and since $\text{Re}(i k) < 0$, one has the following limiting functional form of $\bar{F}(k, r)$:

$$\begin{aligned} \bar{F}(k, r) \sim & k \frac{i}{k r} e^{i k r} \frac{1}{2} k^{-3} \sum_1^* \left[u_1 e^{-\nu_1} e^{(\nu_1 - i k) r} \left\{ -\nu_1^2 r - i k \nu_1 r + \frac{\nu_1^3 r}{\nu_1 - i k} \right\} \right. \\ & + k \frac{-i}{k r} e^{-i k r} \left(\frac{-i}{2} \right) k^{-3} \sum_1^* \left[u_1 e^{-\nu_1} e^{(\nu_1 + i k) r} \right. \\ & \left. \cdot \left\{ \nu_1^2 r - i k \nu_1 r - \frac{\nu_1^3 r}{\nu_1 - i k} \right\} \right] + \\ & + \frac{i}{2} (2 + \bar{s}_1) \frac{1}{C_+^{(1)}} \frac{i}{k r} e^{i k r} - k C_+^{(2)} \frac{i}{k r} e^{i k r} B(k), \end{aligned}$$

or

$$\begin{aligned} \bar{F}(k, r) \sim & \frac{i}{k^2} \sum_{\{1_0\}}^* \left[u_{1_0} \nu_{1_0} \exp(\nu_{1_0} (r - 1)) \right] - \frac{1}{k r} e^{i k r} \left[\frac{i}{2} (2 + \bar{s}_1) / C_+^{(1)} + \right. \\ & \left. + i k C_+^{(2)} B(k) \right], \end{aligned}$$

where $\{1_0\} \equiv \{1 : 0 \geq \text{Re}(\nu_1) \geq \text{Re}(\nu_{1'}) \text{ for all } 1'\} \quad (3.4.3)$

Since the asymptotic form for large r is determined mainly by the exponential factor, one can write

$$\tilde{F}(k, r) \sim \begin{cases} \frac{i}{k^2} \sum_{\{1_0\}}^{\#} u_{1_0} v_{1_0} \exp(v_{1_0}(r-1)), & \text{if } \operatorname{Re}(v_{1_0}) > \operatorname{Re}(ik) \\ \frac{-1}{k r} e^{ikr} \left[\frac{1}{2}(2 + s_1^2)/C_+^{(1)} + ik C_+^{(2)} B(k) \right], & \text{if } \operatorname{Re}(ik) > \operatorname{Re}(v_{1_0}) \end{cases}$$

where $\{1_0\}$ is defined by (3.4.3).

Since $g_0(r) \rightarrow 1$ as $r \rightarrow \infty$, the asymptotic form of deviation factor is

$$\begin{aligned} 10Z_{\chi_1^0} &= \frac{1}{3} \tilde{g}_0^{-1/2}(r) P_2^2(\cos \theta) \operatorname{Re} \left[-e^{+i2\phi} \tilde{F}(k, r) \right] \sim \\ &\sim \begin{cases} P_2^2(\cos \theta) \operatorname{Re} \left[-e^{+i2\phi} \frac{i}{3 k^2} \sum_{\{1_0\}}^{\#} \left\{ u_{1_0} v_{1_0} \exp(v_{1_0}(r-1)) \right\} \right], & \text{if } \operatorname{Re}(v_{1_0}) > \operatorname{Re}(ik) \\ P_2^2(\cos \theta) \operatorname{Re} \left[-e^{+i2\phi} \left(\frac{-1}{k r} \right) e^{ikr} \left\{ \frac{1}{2}(2 + s_1^2)/C_+^{(1)} + ik C_+^{(2)} B(k) \right\} \right], & \text{if } \operatorname{Re}(ik) > \operatorname{Re}(v_{1_0}) \end{cases} \end{aligned} \quad (3.4.4)$$

where $\operatorname{Re}(v_{1_0})$, $\operatorname{Re}(ik) < 0$, and $B(k)$ is defined by (3.3.29D).

Even if in the O-Z approximation for density correlation function the v_{1_0} 's can be purely imaginary and have no real part, the real parts of the v_{1_0} 's should be negative in reality, so that the integral for the compressibility constant (3.2.6) may converge. In fact, the ad hoc recipe (3.2.20)' had to be introduced for this, when the v_{1_0} 's had become purely imaginary for the second-order approximation of the P-Y equation for hard spheres in the subsection (iii) of section 3.2). Thus, by all means, the deviation factor decays exponentially for large r , and the hermitian boundary condition at infinity for the differential operator $(\hat{L}_r + r^{-2} \hat{L}_\theta)$ in (2.2.16A, B) is confirmed.

As mentioned before in the section 3.2), $v_{1_0}^{-1}$ is related to the correlation length. If there exists such a phase transition that the compressibility blows up at this transition, the correlation length becomes very large or v_{1_0} becomes very small near this transition, as one can see in (3.2.11). This phenomenon is explained by the clustering tendency of molecules

in the vicinity of the gas-liquid phase transition [ZER, STA]. Thus near the phase transition one can take such a value of k :

$$\operatorname{Re}(i k) < \operatorname{Re}(\nu_1) < 0 \quad \text{for } |k| \text{ not so small,}$$

and the asymptotic form of deviation factor is determined by the first one in (3.4.4), which hardly decays because of the smallness of $\operatorname{Re}(\nu_1)$ as r increases. This implies that the distortion effect of shear flow on the nonequilibrium correlation function becomes of very long range at the gas-liquid phase transition.

- (ii) Shear-rate dependence of the deviation factor for the shear rate much smaller than the inverse correlation length ($|k| \ll |\nu_1| \neq 0$ for all 1)

The deviation factor χ_1^{IOZ} given by (3.3.30B) may be written conveniently as follows:

$$\chi_1^{\text{IOZ}} = \frac{1}{3} \tilde{g}_0^{-1/2}(r) P_2^2(\cos \theta) \operatorname{Re} \left[-e^{+i2\phi} \tilde{F}(k, r) \right]$$

with

$$\tilde{F}(k, r) = i p(k, r) + i b(k, r) + i q(k, r) B(k)$$

$$i p(k, r) = -i 2 k j_2(kr) \operatorname{IOZ} \tilde{N}_A^r(k) + i 2 k n_2(k, r) \operatorname{IOZ} \tilde{J}_A^r(k)$$

$$i b(k, r) = i (1 + \delta_{4,r}) \frac{1 + 5/2}{C_+^{(1)}} h_2^{(1)}(k, r)$$

$$i q(k, r) = -i k (C_+^{(1)} + C_+^{(2)}) n_2(k, r) + k (C_+^{(1)} - C_+^{(2)}) j_2(k, r)$$

$B(k)$ defined by (3.3.29D).

(3.4.5)

Since r is assumed not to be large one may expand $p(k,r)$, $b(k,r)$, and $q(k,r)$ in power series in k , which is performed in App. 1) to the fourth order.

The factor $B(k)$ in the third term of $\overset{0}{F}(k,r)$ needs some further discussion. It is defined by

$$B(k) \equiv \frac{1}{C_+(1)} \text{IOZ} \overset{\infty}{H}_A^{(1)}(k) .$$

It includes the following typical rational function:

$$(\nu_1 + i k)^{-n} \quad \text{for } n = 1, 2, \quad (3.4.6)$$

as can be seen in (3.3.29B or D).

In expanding (3.4.6) in power series one should consider its convergence. For $|k/\nu_1| < 1$ (or > 1) the rational function (3.4.6) should be expanded in k/ν_1 (or ν_1/k) to converge. Since in this subsection it is assumed that $|k| \ll |\nu_1| \neq 0$ for all l , one can expand the rational function (3.4.6) in the following way:

$$\begin{aligned} (\nu_1 + i k)^{-n} &= \nu_1^{-n} (1 + i k/\nu_1)^{-n} \\ &= \nu_1^{-n} \left\{ 1 - n (i k/\nu_1) + \frac{n}{2} (n+1) (i k/\nu_1)^2 - \right. \\ &\quad \left. - \frac{n}{6} (n+1) (n+2) (i k/\nu_1)^3 + \right. \\ &\quad \left. + \frac{n}{24} (n+1) (n+2) (n+3) (i k/\nu_1)^4 - \dots \right\} . \end{aligned} \quad (3.4.7)$$

In this subsection it is sufficient to take the second-order approximation of (3.4.7). For the later use, however, one takes the terms to the fourth order in k . For $n = 1, 2$ one has from (3.4.7)

$$\begin{aligned}
 (v_1 + i k)^{-1} &\approx v_1^{-1} \left\{ 1 - i k/v_1 - (k/v_1)^2 + i (k/v_1)^3 + (k/v_1)^4 \right\} \\
 (v_1 + i k)^{-2} &\approx v_1^{-2} \left\{ 1 - 2 i k/v_1 - 3 (k/v_1)^2 + 4 i (k/v_1)^3 + \right. \\
 &\quad \left. + 5 (k/v_1)^4 \right\} .
 \end{aligned}
 \tag{3.4.7}'$$

On substituting (3.4.7)' into (3.3.29B) and performing some calculation one obtains the fourth-order approximation in k :

$$\text{IOZ } H_A^{(1)}(k) \approx \frac{i}{2} k^{-3} \sum_1^{\#} u_1 \left\{ 3 + \left(\frac{1}{2} - v_1^{-1}\right) k^2 + \left(\frac{1}{8} - \frac{1}{2} v_1^{-1} + v_1^{-2} - v_1^{-3}\right) k^4 \right\} ,$$

or more compactly

$$\text{IOZ } H_A^{(1)}(k) \approx 3 i k^{-3} H_0 (1 + H_2 k^2 + H_4 k^4)$$

with
$$H_0 \equiv \frac{1}{2} \sum_1^{\#} u_1 = 1/2 \sum_1^{\#} (1^+)$$

$$H_2 \equiv \frac{1}{12 H_0} \sum_1^{\#} u_1 (1 - 2 v_1^{-1})$$

$$H_4 \equiv \frac{1}{48 H_0} \sum_1^{\#} u_1 (1 - 4 v_1^{-1} + 8 v_1^{-2} - 8 v_1^{-3}) , \tag{3.4.8}$$

where the linear and the third-order term don't appear in the parentheses. It could be roughly surmised from the original definition of the integral (3.3.21A) in the following way: For $|k| \ll |v_1|$ the function $(\sqrt{v_1} r)^{-1} \sim \exp(v_1 r)$ decays faster than the spherical Hankel function $h_2^{(1)}(k r)$ in (3.3.21A) and $h_2^{(1)}(k r) = j_2(k r) + i n_2(k r)$ may be expanded in power series in the integrand. Since $j_2(k r) \sim (k r)^2 \cdot \{\text{even function of } k\}$ and $n_2(k r) \sim (k r)^{-3} \cdot \{\text{even function of } k\}$ for small $|k r|$, one has

$$\begin{aligned}
 h_2^{(1)}(k r) &= j_2(k r) + i n_2(k r) \\
 &\sim (k r)^{-3} \left\{ \dots + \dots k^2 + \dots k^4 + \dots k^5 + \dots \right\} ,
 \end{aligned}$$

where ".." denotes the expansion coefficients, and the first- and the third-order term are missing.

It should be noticed that the expansion coefficients H_0 , H_2 , and H_4 in (3.4.8) are real numbers, for the u_1 's and the v_1 's appear always in complex-conjugate pairs in the summation for the density correlation function as mentioned in section 3.2).

Now the fourth-order approximation of $B(k)$ may be obtained from (3.4.8) and (app. 1.6):

$$\begin{aligned} B(k) &= (1/C_+^{(1)}) \text{IOZ} \prod_A^{(1)}(k) \\ &\approx \frac{1}{3} k^3 C_0^{(1)} \left\{ 1 + C_2^{(1)} k^2 + C_4^{(1)} k^4 \right\} \\ &\quad \cdot 3 i k^{-3} H_0 \left\{ 1 + H_2 k^2 + H_4 k^4 \right\} \end{aligned}$$

or compactly

$$B(k) \approx B_0 (1 + B_2 k^2 + B_4 k^4)$$

with $B_0 \equiv C_0^{(1)} \cdot H_0$

$$B_2 \equiv C_2^{(1)} + H_2$$

$$B_4 \equiv C_4^{(1)} + C_2^{(1)} \cdot H_2 + H_4, \quad (3.4.9)$$

where B_0 , B_2 , and B_4 are real numbers, and H_0 , H_2 , and H_4 are given by (3.4.8), and $C_0^{(1)}$, $C_2^{(1)}$, and $C_4^{(1)}$ by (app. 1.6).

The function $F(k,r)$ defined in (3.4.5) now may be expressed in power series in k to the fourth order by using the fourth-order representations for $p(k,r)$, $b(k,r)$, $q(k,r)$, and $B(k)$ calculated in (app. 1.5, 8, 9) and (3.4.9), respectively:

$$\overset{\circ}{F}(k, r) = i p(k, r) + i b(k, r) + i q(k, r) B(k)$$

$$\cong i F_0(r) + i F_2(r) k^2 + i F_4(r) k^4$$

$$\text{with } F_0(r) \equiv p_0(r) + b_0(r) + q_0(r) B_0$$

$$F_2(r) \equiv p_2(r) + b_2(r) + B_0 \{ q_2(r) + q_0(r) B_2 \}$$

$$F_4(r) \equiv p_4(r) + b_4(r) + B_0 \{ q_4(r) + q_2(r) B_2 + q_0(r) B_4 \}, \quad (3.4.10)$$

where the linear and the third-order term in k have been exactly cancelled and don't appear. Since $k = \exp(i\pi/4) \sqrt{\gamma |\gamma_T|}$ from (3.3.5, 24), $\overset{\circ}{F}(k, r)$ can be rewritten as

$$\overset{\circ}{F}(k, r) \cong i F_0(r) + i F_2(r) (i 2 \gamma |\gamma_T|) - i F_4(r) (2 \gamma \gamma_T)^2$$

$$= i F_0(r) - F_2(r) (\gamma |\gamma|) - i F_4(r) (\gamma \gamma)^2$$

$$(\gamma_T = \gamma/2 \text{ from (2.2.5)})$$

$$(3.4.10)'$$

Then the deviation factor defined in (3.4.5) becomes:

$$IOZ \chi_1^0 \cong \frac{1}{3} \hat{g}_0^{-1/2}(r) P_2^2(\cos \theta) \operatorname{Re} \left[-e^{+i2\phi} \{ i F_0(r) - F_2(r) (\gamma |\gamma|) - i F_4(r) (\gamma \gamma)^2 \} \right]$$

$$\cong \frac{1}{3} \hat{g}_0^{-1/2}(r) P_2^2(\cos \theta) \{ F_0(r) \sin 2\phi + F_2(r) (\gamma |\gamma|) \cos 2\phi \}$$

$$\text{for small } |k| = \sqrt{\gamma \gamma} \ll |\gamma_1| \neq 0 \text{ for all } 1, \quad (3.4.11)$$

where $F_0(r)$, $F_2(r)$, and $F_4(r)$ are real functions, as can be seen in (3.4.10), and the term quadratic in γ has been neglected.

The limiting expression (3.4.11) is linear in the shear rate γ . The limiting features of viscosity coefficients are different from that of the deviation factor (3.4.11). For example, in the shear viscosity the linear term of γ in (3.4.11) vanishes, for the Cartesian tensor for shear pressure is

$$x y / r^2 = 1/2 \sin^2 \theta \sin 2 \phi ,$$

which includes the azimuthal function $\sin 2 \phi$ orthogonal to $\cos 2 \phi$ in (3.4.11).

In the viscosity problem one should preserve the quadratic term of γ in $\bar{F}(k, r)$ to see the nontrivial limiting feature for small shear rate.

One can examine the deviation in the x-y plane from the result (3.4.11): Since $\theta = \pi/2$ in the x-y plane, one has

$$(\text{deviation in x-y plane}) = (\tau |\gamma|/2) g_0(r) \cdot {}^{102} \chi_1^0(r, \pi/2, \phi) \quad \text{from (3.4.0)}$$

$$\begin{aligned} &\approx (\tau |\gamma|/2) g_0^{A/2} g_0 \left\{ F_0(r) \sin 2 \phi + \right. \\ &\quad \left. + F_2(r) (\tau |\gamma|) \cos 2 \phi \right\} , \end{aligned}$$

where the relation $P_2^2(\cos \frac{\pi}{2}) = 3$ has been used. The above expression may be written in another form:

$$\begin{aligned} (\text{deviation in x-y plane}) &\approx \frac{\tau \gamma}{2} g_0^{A/2} g_0 F_0(r) \sqrt{1 + \tau^2 \gamma^2 (F_2(r)/F_0(r))^2} \cdot \\ &\quad \cdot \sin \left\{ 2 \phi + 2 \phi_0(r) \right\} \end{aligned}$$

with

$$\begin{aligned} \tan 2 \phi_0(r) &= \tau \gamma F_2(r)/F_0(r) \\ -\frac{\pi}{2} &< 2 \phi_0(r) < \frac{\pi}{2} , \end{aligned} \quad (3.4.12)$$

where $\phi_0(r)$ depends on the radial variable r .

If $\gamma F_0(r) > 0$ (or < 0), two maxima (or minima) of the deviation occur in the directions of angles $\frac{\pi}{4} - \phi_0(r)$ and $\frac{5}{4}\pi - \phi_0(r)$ to the x axis. As r changes, this deviation angle varies. Accordingly the maxima of deviation are twisted. This implies that the ridges of pair-correlation function are distorted under shear flow, whereas they form concentric

shells in equilibrium. One can calculate the deviation angle explicitly without any particular difficulties. There one has only to perform some tedious calculation.

The crucial point for the limiting feature (3.4.11) is the power expansion (3.4.7) which demands the condition $|k| \ll |\nu_1|$ for its convergence. Since ν_1 defined by (3.4.3) is mostly different from zero even near a gas-liquid phase transition and one can take the shear rate arbitrarily small, the "ultimate" limiting behavior of deviation factor for the shear rate approaching to zero may be given by the result (3.4.11). However, $|k|$ can be much larger than the inverse correlation length but so small that any rational function containing no ν_1 's in its denominator may be expanded in power series in k . This case is handled in the next subsection.

(iii) Shear-rate dependence of the deviation factor for the small shear rate ($|k| < 1$) but much larger than the inverse correlation length ($|k| \gg |\nu_1|$)

To come to the point it suffices to consider the second-order approximation for equilibrium density correlation function, (3.2.5) or (3.2.13) according to $\nu^2 \geq 0$ or $\nu^2 < 0$, respectively and denotes

$$\tilde{s}(r) = \sum_1^{II} (u_1/r) e^{\nu_1(r-1)} \equiv \begin{cases} \sum_1^{(3.2.5)} (u_1/r) e^{\nu_1(r-1)} \equiv \frac{u}{r} e^{-\nu(r-1)} \\ \text{from (3.2.5), if } \nu \geq 0 \\ \sum_1^{(3.2.13)} (u_1/r) e^{\nu_1(r-1)} \equiv \sum_{l=1}^2 (u_l/r) e^{\nu_l(r-1)} \\ \text{from (3.2.13), if } \nu_1^2 = \nu_2^2 < 0 \end{cases} \quad (3.4.13)$$

As one can see in (3.2.11, 12), all v_1 's become very small in the second-order approximation for $\hat{s}(r)$, when the compressibility K_T blows up under the assumption of existence of such a phase transition. In this situation one can take some small values of $|k| < 1$, which are still much larger than $|v_1|$. For such values of k the power expansion (3.4.7) in (k/v_1) does fail to converge and one should try to expand the rational function $(v_1 + i k)^{-n}$ in power series in (v_1/k) , which is the point of this subsection.

Thus one assumes in this subsection that all v_1 's in (3.4.13) are very small, which implies a large value of the compressibility, where the existence of such a phase transition is simply assumed, to obtain the following inequalities:

$$|v_1| \ll |k| < 1 \quad \text{for all } 1. \quad (3.4.14)$$

All the procedures are similar to those performed in the last subsection (ii) except for the power expansion of the rational function (3.4.6). When $|k| \gg |v_1|$, the expansion of (3.4.6) can be made in the following way

$$\begin{aligned} (i k + v_1)^{-n} &= (i k)^{-n} \left\{ 1 - i v_1/k \right\}^{-n} \\ &= (i k)^{-n} \left\{ 1 + n (i v_1/k) + \frac{n}{2} (n+1) (i v_1/k)^2 + \right. \\ &\quad \left. + \dots \right\}, \end{aligned} \quad (3.4.15)$$

which converges rapidly.

The expansion (3.4.15) may be substituted into the expression for $N(k)$ in (3.3.29D) to give the following approximation to the first-order in (v_1/k) , introducing the definition (3.4.13),

$$N(k) \cong \sum_I^{II} u_1 \left\{ 3 - 3 v_1 - v_1^2 - i k (1 - v_1) - i v_1^2 (4 + v_1)/k \right\}.$$

Since $|v_1| \ll |k| < 1$, one has $|v_1^3/k| \ll |v_1^2| \ll |v_1 k| \ll |k^2|$ and $|v_1^2/k| \ll |v_1| \ll |k|$. Thus the terms smaller than the value in the order of $|v_1|$ may be neglected in the summand above to obtain the approximation in the order of k :

$$N(k) \cong \sum_I^{II} u_1 \{ 3 - 3 v_1 - i k \} ,$$

or

$$N(k) \cong N_0^< (1 - i N_1^< k)$$

with

$$N_0^< \equiv \sum_I^{II} u_1 (3 - 3 v_1) = -3 \left\{ \frac{d}{dx} s(x) \right\}_{x=1^+} \equiv -3 s'(1^+) =$$

$$= -3 g_0'(1^+)$$

$$N_1 \equiv (1/N_0^<) \sum_I^{II} u_1 = (1/N_0^<) (g_0(1^+) - 1) , \quad (3.4.16)$$

where "<" means the condition for v_1 's, (3.4.14).

It is here noted that $N_0^<$ and $N_1^<$ in (3.4.16) are real numbers, for u_1 's and v_1 's in the summand occur always in complex-conjugate pairs as discussed in the section 3.2).

The limiting form of the function $\tilde{F}(k, x)$ defined by (3.4.5) may be obtained in the similar way to that made in the last subsection except for $B(k)$, which may be now calculated from (3.3.29D) and (3.4.16) as follows

$$B(k) = N(k)/Q(k)$$

$$\cong N_0^< (1 - i N_1^< k) Q_0^{-1} \{ 1 - i k + Q_2 k^2 \}^{-1}$$

or compactly

$$B(k) \cong B_0^< (1 + i B_1^< k)$$

with

$$\begin{aligned} \bar{\theta}_0 &\equiv N_0^</math>
$$\bar{\theta}_1 \equiv 1 - N_1^</math>
(3.4.17)$$$$

where the linear approximation in k has been made, and $\bar{\theta}_0^</math> and $\bar{\theta}_1^</math> are real numbers, as can be deduced from (3.4.16).$$

The linear term in k is present in (3.4.17), whereas it was exactly canceled in the expression for $B(k)$ (3.4.9) in the last subsection. Now one may follow the same procedure stated in (3.4.10) in the last subsection, replacing $B(k)$ by that given by (3.4.17), to obtain the following asymptotic form for $\bar{F}(k, r)$:

$$\begin{aligned} \bar{F}(k, r) &= i p(k, r) + i b(k, r) + i q(k, r) B(k) \\ &\approx i \left\{ p_0(r) + p_2(r) k^2 \right\} + i \left\{ b_0(r) + b_2(r) k^2 \right\} + \\ &\quad + i \left\{ q_0(r) + q_2(r) k^2 \right\} \bar{\theta}_0^</math>$$

or compactly

$$\begin{aligned} \bar{F}(k, r) &\approx i F_0^</math>$$

with

$$F_0^</math>$$

$$F_1^</math>$$

$$k \equiv k_+ \equiv e^{i\pi/4} \sqrt{\tau|\gamma|} \quad \text{defined in (3.3.5) ,} \quad (3.4.18)$$

where the terms quadratic in k have been neglected.

On replacing the $\bar{F}(k, r)$ in (3.4.5) by (3.4.18) one has for the deviation factor

$$\begin{aligned} 10Z \chi_1^0 &\approx \frac{1}{3} \tilde{\theta}_0^{-1/2}(r) P_2^2(\cos \theta) \operatorname{Re} \left[e^{i2\phi} \left\{ F_1^<(r) \sqrt{\tau|\gamma|/2} + i(F_0^<(r) + F_1^<(r) \sqrt{\tau|\gamma|/2}) \right\} \right] \\ &= \frac{1}{3} \tilde{\theta}_0^{-1/2}(r) P_2^2(\cos \theta) \left\{ (F_0^<(r) + F_1^<(r) \sqrt{\tau|\gamma|/2}) \sin 2\phi - \right. \\ &\quad \left. - F_1^<(r) \sqrt{\tau|\gamma|/2} \cos 2\phi \right\} \end{aligned}$$

$$\text{for small } |k| = \sqrt{\tau|\gamma|} \gg |\gamma_1| \quad \text{for all } 1, \quad (3.4.19)$$

where $F_0^<(r)$ and $F_1^<(r)$ are real functions.

The expression (3.4.19) is not exact in its power expansion in k (or $|\gamma|^{1/2}$), but includes the error occurring in the course of approximation for $N(k)$ in (3.4.16). For example the first-order term in k (or $|\gamma|^{1/2}$) may contain further the quantities proportional to $\gamma_1 k$, $\gamma_1^2 k$, $\gamma_1^3 k$, and so on. The sum of these further terms linear in k are in the order of $|\gamma_1 k| \ll |k^2| < |k| < 1$, which is still much smaller than the linear (in $|\gamma|^{1/2}$) term in (3.4.19) and may be neglected. The total error in (3.4.24) is about in the order of

$$|k^2| + |\gamma_1^2/k|.$$

Since $|\gamma_1^2/k| \ll |\gamma_1/k| \ll 1$, the term proportional to $|k|^{-1} = |\tau\gamma|^{-1/2}$ may be neglected in (3.4.19).

The deviation factor (3.4.19) derived in this subsection contains a square-root- γ term, whereas the deviation factor (3.4.11) derived in the last subsection is linear in γ . The square-root- γ term of deviation factor (3.4.19) was caused by the different condition for k and γ_1 from that in the last subsection:

$$|k| = \sqrt{\tau|\gamma|} \ll |\gamma_1| \neq 0 \quad \text{for all } 1, \text{ in the last subsection,}$$

and

$$1 > |k| \gg |\gamma_1| \quad \text{for all } 1, \text{ in this subsection.}$$

Thus it may be pointed out that the behavior of nonequilibrium correlation function under shear flow (with homogeneous density and temperature) is determined not by the shear rate alone but by the ratio of the shear rate to the inverse correlation length. The deviation itself is given by

$$\begin{aligned}
 (\text{deviation}) &= \frac{\tau \dot{\gamma}}{2} g_0(r) \text{IOZ } \chi_1^0 && \text{from (3.4.0)} \\
 &\approx \frac{1}{6} \tau \dot{\gamma} g_0^{1/2} g_0 P_2^2(\cos \theta) \left[\left\{ F_0^<(r) + \sqrt{\tau |\dot{\gamma}|/2} F_1^<(r) \right\} \sin 2\phi - \right. \\
 &\quad \left. - \sqrt{\tau |\dot{\gamma}|/2} F_1^<(r) \cos 2\phi \right]_{\text{from (3.4.19)}} && (3.4.20)
 \end{aligned}$$

(iv) Shear-rate dependence of the deviation factor in the large shear-rate limit

For large shear rate the consideration about the Couette-flow seems to be meaningless, since the turbulence is expected to occur. Nevertheless one may try to extract some qualitative feature of the nonequilibrium pair-correlation function under shear flow with large shear rate, under the assumption that the shear flow is still laminar, i.e. the fluid moves as if it were in layers with different velocities, even for large shear rate.

In order to see the behaviour of the deviation factor for large shear rate the expression (3.3.30A) is appropriate and the function $\tilde{F}(k, r)$ containing all the shear-rate dependence is given by (3.4.1):

$$\begin{aligned} \tilde{F}(k, r) = & k h_2^{(1)}(kr) \cdot \text{IOZ}_{\frac{1}{4}A}^r H_A^{(2)}(k) + k h_2^{(2)}(kr) \cdot \left\{ \text{IOZ}_{\frac{1}{4}A}^{\infty} H_A^{(1)}(k) - \text{IOZ}_{\frac{1}{4}A}^r H_A^{(1)}(k) \right\} + \\ & + \frac{i}{2} (1 + \delta_{1,p}) (2 + S_1) h_2^{(1)}(kr) \left\{ \frac{1}{2} T_*^{-1} w'(1^+) h_2^{(1)}(k) + \left(\frac{d}{dp} h_2^{(1)}(kp) \right)_{p=1} \right\}^{-1} - \\ & - k h_2^{(1)}(kr) \left\{ \frac{1}{2} T_*^{-1} w'(1^+) h_2^{(2)}(k) + \left(\frac{d}{dp} h_2^{(2)}(kp) \right)_{p=1} \right\} B(k), \end{aligned} \quad (3.4.21)$$

where $B(k)$ is defined in (3.3.29D) and the $C_+^{(1,2)}$ are written explicitly from their definitions in (3.3.13B). Since $\text{Re}(ik) = \text{Re}(i e^{i\pi/4} \sqrt{\tau_1 \tau_1}) < 0$ and $r(>1)$ is assumed not to be large, by making use of the results (3.3.29A, B, D) for the integrals in the first two terms and $B(k)$, and taking the asymptotic form of each term for large k , one obtains

$$\begin{aligned} \hat{F}(k, r) \sim & k \frac{1}{2r} e^{ikr} \frac{1}{2} k^{-3} \sum_{\ell}^{\#} \left\{ u_{\ell} e^{-\gamma_{\ell}} \cdot e^{(\gamma_{\ell} - ik)r} \cdot i k (1 - \gamma_{\ell} r) \right\} + \\ & + k \cdot \frac{-i}{kr} e^{-ikr} \cdot \frac{-i}{2} k^{-3} \sum_{\ell}^{\#} \left\{ u_{\ell} e^{-\gamma_{\ell}} \cdot e^{(\gamma_{\ell} + ik)r} \cdot i k (1 - \gamma_{\ell} r) \right\} + \\ & + i(1 + \delta_{\ell, r}) \frac{i(1 + \frac{\gamma_{\ell}}{2})}{kr} e^{ikr} \cdot \left\{ \frac{1}{2} T_{*}^{-1} \omega'(1^{+}) \cdot \frac{1}{k} e^{ik} - e^{ik} \right\}^{-1} - \\ & - k \frac{1}{kr} e^{ikr} \cdot \left\{ \frac{1}{2} T_{*}^{-1} \omega'(1^{+}) \cdot \frac{-i}{k} e^{-ik} - e^{-ik} \right\} \cdot \left\{ -ik \sum_{\ell}^{\#} u_{\ell} (1 - \gamma_{\ell}) \right\} (Q_0 Q_3 i k^3) \sim \\ \sim & \frac{-i}{k^2 r} \sum_{\ell}^{\#} \left\{ u_{\ell} e^{\gamma_{\ell} (r-1)} (1 - \gamma_{\ell} r) \right\} \quad \text{for } r > 1, \end{aligned}$$

where the terms decaying exponentially with increasing $|k|$ are neglected.
Since

$$\begin{aligned} g_0'(r) &\equiv \frac{d}{dr} g_0(r) = \frac{d}{dr} \tilde{S}(r) \approx \frac{d}{dr} \sum_{\ell}^{\#} \left\{ (u_{\ell}/r) e^{\gamma_{\ell} (r-1)} \right\} \quad \text{for } r > 1 \\ &= - \sum_{\ell}^{\#} \left\{ (u_{\ell}/r^2) e^{\gamma_{\ell} (r-1)} (1 - \gamma_{\ell} r) \right\}, \end{aligned}$$

the above asymptotic form for $\hat{F}(k, r)$ may be rewritten as

$$\hat{F}(k, r) \sim \frac{r}{\tau |\gamma|} g_0'(r) \quad \text{for large } |k|, \text{ and } r > 1, \quad (3.4.22)$$

where the relation $k^2 = \left\{ e^{i\pi/4} \sqrt{\tau |\gamma|} \right\}^2 = i \tau |\gamma|$ has been used.

The function $\hat{F}$ in (3.3.30A) is replaced by that given by (3.4.22) to give the asymptotic form for the deviation factor ($r > 1$)

$$\begin{aligned} {}^{102} \chi_1^0 &\sim \frac{-1}{\tau \gamma} \frac{r}{3} \hat{g}_0^{-1/2}(r) g_0'(r) P_2^2(\cos \theta) \cos 2\phi \\ &= \frac{-1}{\tau \gamma} \frac{2r}{3} \left\{ g_0^{1/2}(r) \right\}' \cdot P_2^2(\cos \theta) \cos 2\phi. \end{aligned} \quad (3.4.23)$$

Here it is noted that the deviation factor given by (3.4.28) decreases inversely as the shear rate increases, but the deviation itself approaches to a function independent of shear rate:

$$g_0(r) \approx g_0(r) \left\{ (\tau \gamma_d)^{102} \chi_1^0 \right\} \quad \text{from (3.4.0)}$$

$$\xrightarrow{r \gg 1} -\frac{\pi}{9} \left\{ g_0^{3/2}(r) \right\}' \cdot p_2^2(\cos \theta) \cos 2\phi \quad \text{as } |\gamma| \rightarrow \infty, \quad (3.4.24)$$

where the relations $\gamma_d = \gamma/2$ and $g_0(r) \left\{ g_0^{1/2}(r) \right\}' = \frac{1}{3} \left\{ g_0^{3/2}(r) \right\}'$ have been used.

At $r=1$, the third term in the expression for $\overset{\circ}{F}(k, r)$ stated above (3.4.22) is dominant among all the other terms and one has

$$\begin{aligned} \overset{\circ}{F}(k, 1) &\sim -(2+s_1^>)k^{-1} \left\{ \frac{1}{2} T_*^{-1} w'(1^+) k^{-1} - 1 \right\}^{-1} \\ &\sim (2+s_1^>)k^{-1} \\ &= (2+s_1^>)e^{-i\pi/4} (\tau|\gamma|)^{-1/2}. \end{aligned} \quad (3.4.25)$$

Therefore the deviation factor at the hard core is proportional to $(\tau|\gamma|)^{-1/2}$ for large shear rate and decays very slowly.

The deviation itself at the hard core is in proportion to $(\tau|\gamma|)^{1/2}$ for large values of shear rate, whereas it approaches to a certain value independent of shear rate for $r > 1$. This asymptotic form of the deviation factor at the hard core is closely related to that of the viscosity coefficients.

(v) Remarks on the problem of convergence at the liquid-gas and the fluid-to-solid-like phase transition

The most important implication of the nonanalytic behavior (3.4.19) is that the traditional perturbation expansion of g in power series in the (total) shear rate $[KIR2, RIC, ZWA, LOW]$ does not converge in the range of shear rate $\sqrt{\kappa\gamma} > |\gamma_1|$. This problem of convergence arose already in expanding the rational function $(i k + \gamma_1)^{-n}$ in power series, where one had to expand it for $|k| > |\gamma_1|$ according to (3.4.15). At the liquid-gas phase transition the compressibility blows up and the inverse correlation length becomes practically zero, even if not absolutely zero, as can be seen in (3.2.7 or 11). Therefore one can say that the traditional perturbation expansion in the (total) shear rate diverges in the "almost" whole range of shear rate at the liquid-gas phase transition. But, as mentioned in the last subsection, the "ultimate" limiting behavior of the deviation factor is analytic even at the liquid-gas phase transition, if the square-root shear rate (multiplied by κ) is smaller than the inverse correlation length which is practically zero at the liquid-gas transition. Thus the small range of shear rate for the analytic behavior (3.4.11) is ignored practically at the liquid-gas phase transition.

Another problem of convergence arises at the fluid-to-solid-like phase transition which will be discussed in sec. 4.3). The first and the second term of the function $\tilde{F}$ of the general solution (3.3.25A,B) for the deviation factor,

$$i(1+\delta_{1,r})\sqrt{g_0(r)}\frac{1}{c_+^{(1)}}h_2^{(1)}(k,r) + k\left(c_+^{(1)}h_2^{(2)}(k,r) - c_+^{(2)}h_2^{(1)}(k,r)\right)\frac{1}{c_+^{(1)}}H_1^{(1)}(k)$$

$$\cong ib(k,r) + iq(k,r)B(k) \quad \text{from (3.4.5),}$$

have something to do with the fluid-to-solid-like phase transition. This phase transition is explained in the relations to viscosity or pressure tensor in sec. 4.3). Here one is interested only in the problem of convergence of the perturbation series with respect to the (total) shear rate. Until now in this section one has assumed tacitly that

$$\omega_1 = \frac{1}{2} \tau_*^{-1} \omega'(1^+) \neq 3, \quad ,$$

in order to expand $1/C_+^{(1)}$ in power series in k , as stated in (app. 1.7A). The value $-\omega'(1^+)$ is the mean force at the hard core in the relative pair configurational space. When $\omega_1 = 3$, the power expansion (app. 1.7) is absolutely invalid. The two terms stated above become in this situation:

$$i b(k, r) + i q(k, r) B(k)$$

$$\approx \left[\{ N_0 q_0(r) - 6(2 + s_1^2)/r^3 \} (1 - ik) + \right. \\ \left. + \{ N_0 N_2 q_0(r) + N_0 q_0(r) - (2 + s_1^2)(r^{-1} - 3r^{-3}) \} k^2 \right] / [-2k^2(1 - ik)]$$

$$\text{with} \quad k = \exp(i\pi/4) \sqrt{\tau\dot{\gamma}},$$

which is here rewritten from (4.3.3A).

The quantities N_0 and N_2 , and $q_0(r)$ are defined by (4.3.4) and (app. 1.9), respectively. They are independent of k , i.e. the shear rate. The above expression contains a singular term proportional to $1/k^2 = -i/(\tau\dot{\gamma})$ and a nonanalytic term proportional to $k = \exp(i\pi/4) \sqrt{\tau\dot{\gamma}}$ when the rational function $1/(1 - ik)$ is expanded in power series in small k . Here one can see clearly that the traditional perturbation expansion of $(g - g_0)/g_0$ with respect to the shear rate ($\dot{\gamma}$) does not converge at all, when $\omega_1 = 3$. Moreover the deviation factor has the singular term proportional to $1/k^2 = -i/(\tau\dot{\gamma})$ at the fluid-to solid-like phase transition ($\omega_1 = 3$). This singular term is related to the jumping-up of normal-pressure difference just at the moment of switching on the shear strain at the fluid-to-solid-like phase transition. The deviation itself, however, is not singular, as can be seen in (3.4.0).

IV. Viscosity coefficients

The representations for the potential contributions to the shear viscosity and the coefficients for normal pressure differences are obtained explicitly by making use of the results of last chapter. The ansatz (3.1.1) for intermolecular potential is introduced also in this chapter and proves to be very useful. The limiting features of viscosity coefficients are discussed. Especially the viscosity coefficients for hard spheres are given as functions of density and shear rate in their complete explicit form, where the W-T solution for the P-Y equation for hard spheres may be used. At some condition of temperature and density the fluid system shows an exotic behavior in its viscosity coefficients, which is here considered as a fluid-to-solid-like phase transition. The correct condition for this transition is given, and checked by using the W-T solution. Near this fluid-to-solid-like phase transition the square-root- γ term of shear viscosity coefficient is also found, but it is a very short-range behavior.

In the last section the functional dependences of viscosity coefficients on the shear rate will be shown in graphs and their relations to the transition mentioned above are discussed for hard spheres.

In this chapter the kinetic contributions to viscosity coefficients are not considered. It is assumed that in a dense fluid the potential contribution to the pressure tensor is preponderant over the kinetic contribution and the latter may be neglected.

4.1) Non-Newtonian viscosity and the case of hard spheres

A correct expression for the viscosity coefficients will be first derived. For the practical calculation, however, one uses rather the more explicit solution (3.3.30A or B) for deviation factor than the general form (3.3.25A or B). The two expressions (3.3.30A and B) for the deviation factor $^{IOZ}_1^0(\underline{r})$ are the alternative forms of the same one, and may be rewritten from (3.4.5):

$$p_1^0 = ^{IOZ}_1^0 = 3^{-1} \tilde{g}_0^{-1/2}(r) P_2^2(\cos \theta) \operatorname{Re} [-e^{i2\phi} \dot{F}(k, r)]$$

$$\text{with } \dot{F}(k, r) = i p(k, r) + i b(k, r) + i q(k, r) B(k), \quad (4.1.1)$$

where the functions $p(k, r)$, $b(k, r)$, $q(k, r)$, and $B(k)$ are defined in (3.4.5) and (3.3.29D), respectively.

In a homogeneous dense fluid the potential part of pressure tensor may be represented microscopically by using the nonequilibrium pair-correlation function as follows /KIR2/

$$\underline{P}^{\text{pot}} = -n^2 / (2\sigma^3) \int (\underline{r}\underline{r}/r) v'(\underline{r}) g(\underline{r}) d^3r, \quad (4.1.2)$$

where n is the reduced molecular number density per volume σ^3 .

Since the nonequilibrium pair-correlation function of first-order perturbation in the deformation parameter γ_d is

$$g(\underline{r}) = g_0(r) \left(1 + (\tau \gamma_d) \chi_1^0(r, \theta, \phi) \right)$$

from (2.2.7,9) and (3.3.22), one may write the first-order-perturbation expression for the symmetric traceless pressure tensor as

$$P_{\mu\nu}^{\text{pot}} = -n^2 / (2\sigma^3) (\tau \gamma_d) \int (\underline{r}_\mu * \underline{r}_\nu) r v'(r) g_0(r) \chi_1^0 d^3r, \quad (4.1.2)$$

where the Greek subscripts " μ, ν " represent the Cartesian compo-

nents, $\hat{r}_\mu := r_\mu / r$, and $a_\mu * b_\nu$ denotes the symmetric traceless tensor of second rank /HES2,4/ defined by

$$a_\mu * b_\nu = 2^{-1}(a_\mu b_\nu + b_\mu a_\nu) - 3^{-1}\delta_{\mu\nu} a_\mu b_\nu$$

with the summation convention in the repeated indices. This definition implies: $\hat{r}_\mu * \hat{r}_\nu = \hat{r}_\mu \hat{r}_\nu - 3^{-1}\delta_{\mu\nu}$. In the representation (4.1.2) the equilibrium part does not appear for the symmetry of the tensor $\hat{r}_\mu * \hat{r}_\nu$. Here one is interested in the following three quantities of the pressure tensor:

$$\begin{aligned} p_+^{\text{pot}} &:= p_{xy}^{\text{pot}} \\ p_-^{\text{pot}} &:= 2^{-1}(p_{xx}^{\text{pot}} - p_{yy}^{\text{pot}}) \\ p_0^{\text{pot}} &:= 2^{-1}\{ p_{zz}^{\text{pot}} - 2^{-1}(p_{xx}^{\text{pot}} + p_{yy}^{\text{pot}}) \}, \end{aligned} \quad (4.1.3)$$

which may be interpreted as the shear pressure, the normal-pressure difference between x- and y-direction, and the difference of normal pressure in z-direction from the average of those in x- and y-direction, respectively. The corresponding viscosity coefficients are defined by

$$\frac{p_+^{\text{pot}}}{\theta} = -\eta_+^{\text{pot}}(\gamma) \gamma. \quad (4.1.4)$$

Since the Cartesian components corresponding to the pressure components (4.1.3) are

$$\begin{aligned} x*x &= 2^{-1}\sin^2\theta \sin 2\phi \\ 2^{-1}(x*x - y*y) &= 2^{-1}\sin^2\theta \sin 2\phi \\ 2^{-1}\{2*z^2 - 2^{-1}(x*x + y*y)\} &= 4^{-1}(3\cos\theta - 1), \end{aligned} \quad (4.1.5)$$

one can derive immediately from the relations (4.1.2,3,4) the representations for viscosity coefficients defined by (4.1.4):

$$\eta_{\pm 0}^{\text{pot}}(\gamma) = \frac{\tau n^2}{4\sigma^3} \int \left\{ \begin{array}{l} \frac{1}{2} \sin^2 \theta \sin 2\phi \\ \frac{1}{2} \sin^2 \theta \cos 2\phi \\ \frac{1}{4} (3 \cos^2 \theta - 1) \end{array} \right\} \cdot r v'(r) g_0(r) \chi_1^0 d^3 r, \quad (4.1.6)$$

where the relation $\gamma_d = \gamma/2$ has been used.

On replacing the deviation factor in (4.1.6) by the expression (4.1.1) and executing the following integrations in the polar angles θ and ϕ :

$$\int_0^{2\pi} -e^{i2\phi} \left\{ \begin{array}{l} \sin 2\phi \\ \cos 2\phi \\ 1 \end{array} \right\} d\phi = \begin{cases} -i\pi \\ -\pi \\ 0 \end{cases}$$

$$\int_0^\pi P_2^2(\cos \theta) \frac{1}{2} \sin^3 \theta d\theta = \frac{8}{5},$$

one has

$$\eta_{\pm 0}^{\text{pot}}(\gamma) = \frac{2\pi\tau n^2}{15\sigma^3} \operatorname{Re} \left[\begin{Bmatrix} -i \\ -1 \\ 0 \end{Bmatrix} \int_1^\infty r^3 v'(r) g_0(r) \tilde{g}_0^{-1/2}(r) F(k, r) dr \right] \quad (4.1.6)',$$

where the range of integration is restricted to $r \geq 1$, since the hard cores of any pair of molecules cannot be overlapped, and the function $\tilde{g}_0$ defined by (3.3.21D) is continuous at $r=1$ to the right-hand side.

One now introduces the ansatz for intermolecular potential (3.1.1) and writes the factor $v'(r)g_0(r)$ in the integrand of (4.1.6)' in the following way:

$$v'(r)g_0(r) = v'(r)\exp\{-v(r)/T_*\}y(r) \text{ from the def. } y := e^{v/T_*} g_0$$

=

$$= \{v'_0(r) + v'_a(r)\} \exp\{-v_0(r)/T_* - v_a(r)/T_*\} y(r) \text{ from (3.1.1)}$$

$$= -T_* \left(\exp\{-v_0(r)/T_*\} \right)' \exp\{-v_a(r)/T_*\} y(r) + v'_a(r) g_0(r),$$

where $v_0(r)$ is the effective hard-core potential representing the repulsive part of a intermolecular potential, as discussed in § 3.1). Since

$$\left(\exp\{-v_0(r)/T_*\} \right)' = \delta(r-1)$$

and the function $y(r)$ may be assumed to be continuous at $r=1$ (e.g. for the P-Y equation for hard spheres $y(r)$, its first, and its second derivative are continuous at $r=1$ /WER/), one is led to

$$v'_a(r) g_0(r) = -T_* g_0(1^+) \delta(r-1) + v'_a(r) g_0(r), \quad (4.1.7)$$

where of course $v_a(r)$, the attractive part of intermolecular potential, is continuous at $r=1$, as defined in (3.1.1), and the relation

$$\exp\{-v_a(1)/T_*\} y(1) = g_0(1^+)$$

has been used. When (4.1.7) is substituted into (4.1.6)' one obtains

$$\begin{aligned} \eta_{\pm}^{\text{pot}}(\gamma) &= \frac{2\pi T_* \tau \eta^2}{15\sigma^3} \operatorname{Re} \left[\left\{ \begin{matrix} i \\ 1 \\ 0 \end{matrix} \right\} g_0^{1/2}(1^+) F(k, 1) \right] \\ &+ \frac{2\pi \tau \eta^2}{15\sigma^3} \operatorname{Re} \left[\left\{ \begin{matrix} -i \\ -1 \\ 0 \end{matrix} \right\} \int_{R_m/\sigma}^{\infty} r^3 v'_a(r) g_0^{1/2}(r) F(k, r) dr \right] \end{aligned} \quad (4.1.8)$$

and the Newtonian viscosity

$$\eta_{+}^{\text{pot}}(0^+) := \lim_{\gamma \rightarrow 0^+} \eta_{+}^{\text{pot}}(\gamma), \quad (4.1.8)'$$

where R_m/σ , the underlimit of the integral, is the position of minimum of the intermolecular potential $v_{LJ}(r)$, as defined in (3.1.1), and always greater than unity for the Lennard-Jones-type potential, which can be seen in the equation (3.1.2) for the determination of σ . Of course, if the repulsive potential (e.g. r^{-12} -potential) only is present, the second term of (4.1.8) or (4.1.8)' does not appear and one doesn't have to consider R_m . Now one introduces the approximation of the deviation factor, (4.1.1), in order to calculate the viscosity coefficients explicitly. The r -independent factor $F(k,1)$ in the first term of (4.1.8) may be more simplified in the following way: Since

$$\begin{aligned} iq(k,1) &= -ik(C_+^{(1)} + C_+^{(2)})n_2(k) + k(C_+^{(1)} - C_+^{(2)})j_2(k) \text{ from (3.4.5)} \\ &= kC_+^{(1)}h_2^{(2)}(k) - kC_+^{(2)}h_2^{(1)}(k) \text{ from def. (3.3.13,17A)} \\ &= 2i \quad \text{from (3.3.24)} \end{aligned} \quad (4.1.9)$$

and

$$\begin{aligned} b(k,r) &= (1+\delta_{1,r})(1+s_1^>/2)h_2^{(1)}(kr)/C_+^{(1)} \text{ from (3.4.5)} \\ &= (1+\delta_{1,r})(1+s_1^>/2)h_2^{(1)}(kr) \\ &\quad / \{ (2T_*)^{-1}w'(1^+)h_2^{(1)}(k) + \{d/d\rho h_2^{(1)}(k\rho)\}_{\rho=1} \} \\ &= -6(1+\delta_{1,r})(1+s_1^>/2)r^{-3} e^{ik(r-1)} (1-ikr-k^2r^2/3)/Q(k) \end{aligned}$$

$$\text{with } Q(k) \text{ defined in (3.3.29D),} \quad (4.1.10)$$

one has for $F(k,1)$

$$\begin{aligned} F(k,1) &\equiv \overset{\circ}{F}(k,1) = ip(k,1) + ib(k,1) + iq(k,1)B(k) \\ &= ip(k,1) - i6(2+s_1^>)(1-ik-k^2/3)/Q(k) + i2N(k)/Q(k) \\ &\quad \text{from (4.1.9,10 and 3.3.29D)} \\ &= -i6(2+s_1^>)(1-ik-k^2/3)/Q(k) + i2N(k)/Q(k), \end{aligned} \quad (4.1.11)$$

where $p(k,1)=0$ from the definition in (3.4.5).

Substitution of (4.1.11) into (4.1.8) leads to:

$$\begin{aligned} \eta_{\pm}^{\text{pot}}(\gamma) = & \frac{4\pi}{15} (T_* \tau n^2 / \sigma^3) \text{Re} \left[\left\{ \begin{matrix} 1 \\ -i \\ 0 \end{matrix} \right\} g_0^{1/2}(1^+) \left\{ 3(2+s_1^2)(1-ik - \frac{k^2}{3}) - N(k) \right\} \right. \\ & \left. / Q(k) \right] + \\ & + \frac{2\pi}{15} (\tau n^2 / \sigma^3) \text{Re} \left[\left\{ \begin{matrix} -i \\ -1 \\ 0 \end{matrix} \right\} \int_{r_m}^{\infty} r^3 v_a'(r) g_0^{1/2}(r) \overset{\circ}{F}(k, r) dr \right] \end{aligned} \quad (4.1.12)$$

and the Newtonian viscosity

$$\begin{aligned} \eta_+^{\text{pot}}(0^+) &:= \lim_{\gamma \rightarrow 0^+} \eta_+^{\text{pot}}(\gamma) \\ &= \frac{4\pi}{15} (T_* \tau n^2 / \sigma^3) g_0^{1/2}(1^+) / (\Delta w_1) + \\ &+ \frac{2\pi}{15} (\tau n^2 / \sigma^3) \lim_{|k| \rightarrow 0^+} \text{Re} \left[-i \int_{r_m}^{\infty} r^3 v_a'(r) \sqrt{g_0(r)} \overset{\circ}{F}(k, r) dr \right] \end{aligned} \quad (4.1.12)'$$

where $s_1^> := s^>(1^+)$, $r_m := R_m / \sigma$, $k = e^{i\pi/4} (\tau |\gamma|)^{1/2}$, $\Delta w_1 := 3 - w'(1^+) / (2T_*)$, and $N(k)$, $Q(k)$ and $\overset{\circ}{F}(k, r)$ are defined in (3.3.29D and 3.4.5 (or 4.1.1)) respectively. The values of $N(k)$ and $Q(k)$ at $k=0$ are calculated as follows

$$N(0) = 3 \Sigma_1^{\#} u_1 = 3 s_1^>$$

$$Q(0) = 6 \{ 3 - w'(1^+) / (2T_*) \} \text{ from (3.3.29D).}$$

The expression (4.1.12) is the general solution for the potential contribution to viscosity coefficients of first-order perturbation in the deformation parameter γ_d (not the total shear-rate parameter γ !) defined in (2.2.5). The repulsive part of intermolecular potential is replaced by the effective hard core whose effective diameter σ is determined by the equation (3.1.2), and the attractive part of any Lennard-Jones-like potential may be introduced. For the equilibrium pair-correla-

tion function $g_0(r)$ any improved O-Z approximation developed in the section 3.2) may be used.

In the expressions (4.1.12) and (4.1.12)' the main contribution occurs in the first term and the second term is expected to be very small because of the smallness of $v'_a(r)$ over the whole range of r : The function $\tilde{F}^0(k, r)$ decreases exponentially for large r , as can be seen in (3.4.3) of the last chapter. The function $r^3 v'(r)$ is significant only in the vicinity of $r=r_m$ and negligibly small for $r > r_m + \Delta r$, where Δr is the width of significant range for the function $r^3 v'(r)$.

Here one sees again the great advantage of the ansatz (3.1.1) for intermolecular potential. The first term of (4.1.12), the main contribution has been already calculated. As mentioned before, the repulsive part of intermolecular potential may be approximated by the effective hard core whose diameter depends upon both temperature and density. Thus for a fluid system of molecules with the repulsive potential only the second term of (4.1.12) does not appear and one has the following expression for the viscosity coefficients:

$$\begin{aligned} EHS_{\eta_{\pm}^0}^{pot}(\gamma) = & (4\pi T_* \tau n^2) / (15\sigma^3) \operatorname{Re} \left(\left\{ \begin{matrix} 1 \\ -1 \\ 0 \end{matrix} \right\} g_0^{1/2}(1^+) \{3(2+s_1^*) (1-ik-k^2/3) \right. \\ & \left. - N(k) \} / Q(k) \right) \end{aligned} \quad (4.1.13)$$

and the Newtonian viscosity

$$\begin{aligned} EHS_{\eta_+^0}^{pot}(0^+) &:= \lim_{\gamma \rightarrow 0^+} EHS_{\eta_+^0}^{pot}(\gamma) \\ &= (4\pi T_* \tau n^2) / (15\sigma^3) g_0^{1/2}(1^+) / \Delta w_1 \end{aligned} \quad (4.1.13)'$$

with $k = e^{i\pi/4} (\tau |\gamma|)^{1/2}$ from (3.3.5, 23) and (2.2.5)

$$\Delta w_1 := 3 - (2T_*)^{-1} w'(1^+)$$

$$N(k) = \Sigma_1^{\#} u_1 \{ 3 - v_1(3+v_1) - ik(1-v_1) + v_1^2(4+v_1)(v_1+ik)^{-1} - v_1^3(v_1+ik)^{-2} \}$$

$$Q(k) = Q_0 \{ 1 - ik + Q_2 k^2 + iQ_3 k^3 \}$$

$$Q_0 = 18 - 3T_{*}^{-1} w'(1^+)$$

$$Q_2 = \{ T_{*}^{-1} w'(1^+) - 8 \} / Q_0$$

$$Q_3 = 2/Q_0 \quad \text{from (3.3.29D)}$$

$$s_1^> := s^>(1^+) = g_0(1^+) - 1 \quad \text{from (3.3.30C),}$$

where "EHS" means the effective hard sphere. Of course, the expression (4.1.13) may be applied to the true hard sphere fluid, in which the hard sphere diameter σ is merely a constant independent of density and temperature.

It is noticed that in both (4.1.12,13) the viscosity component "0" vanishes, i.e.

$$\eta_0^{\text{pot}}(\gamma) = 0,$$

which is due to the vanishing integration in ϕ executed in the lines just above (4.1.6)'. In the second-order perturbation theory this viscosity component does not disappear, for

$$\begin{aligned} \chi_2 &= g_0^{-1/2} \psi_2 \\ &= g_0^{-1/2} (e^{-i4\phi} \psi_2^{(-4)}(r, \theta) + \psi_2^{(0)}(r, \theta) + e^{i4\phi} \psi_2^{(4)}(r, \theta)) \quad \text{from (2.2.19),} \end{aligned}$$

and one has the ϕ -independent term in the second-order deviation factor χ_2 . This implies that the viscosity component η_0^{pot} survives in the integration in ϕ , as can be seen in (4.1.6). The component of normal pressure difference has the following

form in the second-order perturbation theory:

$$\eta_0^{\text{pot}} \sim \gamma_d f(\gamma_r),$$

where γ_d and γ_r are the deformation and the rotational parameter, respectively, and $f(\gamma_r)$ is a function of γ_r only. The second-order deviation factor χ_2 may be obtained through the similar procedure to that made in the section 3.3).

A more important fact to be noticed is the following: the second-order deviation factor χ_2^0 does not contribute to η_+^{pot} and η_-^{pot} , since the functions $\sin 2\phi$ and $\cos 2\phi$ occurring in their integral representation (4.1.6) are orthogonal to 1 and $\exp(\pm i4\phi)$. Thus the next contribution to the viscosity coefficients, η_+^{pot} and η_-^{pot} , is of third order with respect to the deformation parameter γ_d .

One sees in the expressions (4.1.12 or 13) for the viscosity coefficients a wide variety of their functional dependence on the shear rate ($k = \exp(i\pi/4) (\tau|\gamma|)^{1/2}$) and their complicated relation to the equilibrium pair-correlation function. As can be seen in the following sections, the viscosity coefficients are closely related to the important phenomena in equilibrium, i.e. the gas-liquid and the fluid-solid phase transition.

4.2) Limiting features of the viscosity coefficients

Since in the first-order perturbation theory the viscosity component "0" vanishes, the two components "+" and "-" only are here considered. Similarly to the section 3.4) the following three situations are considered:

- (i) The shear-rate dependence for small shear rate with $|k| \ll |v_1| \neq 0$ for all l ,
- (ii) the shear rate dependence for $|v_1| \ll |k| \leq 1$,
- (iii) the shear-rate dependence for large shear rate, where v_1 's are related to the inverse correlation length as mentioned before.

For the sake of compactness one may introduce the following notation for the integral in the second term of (4.1.12):

$$\langle \dots \rangle \equiv \int_m^\infty r^3 v_B'(r) g_0^{1/2}(r) \{ \dots \} dr \quad (4.2.1)$$

Using the notation (4.2.1) one can rewrite the expression for viscosity coefficients in (4.1.12) as follows

$$\begin{aligned} \eta_{\pm}^{\text{pot}}(\gamma) = & \frac{2\pi}{15\sigma^3} (T_* \tau n^2) \cdot \text{Re} \left[\begin{Bmatrix} 1 \\ -1 \end{Bmatrix} g_0^{1/2}(1^+) \{ -b(k,1) - 2B(k) \} \right] + \\ & + \frac{2\pi}{15\sigma^3} (\tau n^2) \cdot \text{Re} \left[\begin{Bmatrix} -1 \\ -1 \end{Bmatrix} \langle \hat{F}(k,r) \rangle \right] , \end{aligned} \quad (4.2.2)$$

where $b(k,1)$, $B(k)$, and $\hat{F}(k,r)$ are given in (4.1.10), (3.3.29D) and (3.4.5), respectively.

As mentioned in the last section, the contribution to the integral (4.2.1) arises from the short range of r if the factor $\{ \dots \}$ in the integrand behaves normally for large r , i.e. it does not blow up as r increases. Since the function $\hat{F}(k,r)$ decays exponentially for large r , which is shown in (3.4.3), the contribution to the integral $\langle \hat{F}(k,r) \rangle$ from the range of large r may be practically neglected.

If one establishes a cut-off radial distance r_c , over which no significant contribution to $\langle \dot{F}(k, r) \rangle$ occurs, the integral may well be approximated as follows:

$$\langle \dot{F}(k, r) \rangle \approx \langle \dot{F}(k, r) \rangle_c \quad (4.2.3)$$

with the notation

$$\langle \dots \rangle_c \equiv \int_{r_m}^{r_c} r^3 v_a^1(r) g_0^{1/2}(r) \{ \dots \} dr \quad (4.2.4)$$

Practically the cut-off integral (4.2.4) will be used in this and the next subsection.

Many of the results derived in the section 3.4) will be referred to.

- (i) Shear-rate dependence of the viscosity coefficients for the shear rate much smaller than the inverse correlation length
- $$(|k| \ll |V_1| \text{ for all } l)$$
-

This situation corresponds to that of the subsection (ii) of section 3.4). The integral in the second term of (4.2.2) is replaced by the cut-off integral (4.2.3). In this cut-off integral the function $\dot{F}(k, r)$ may be expanded in power series in k , since the integral variable r now is restricted to the region $r < r_c$. This expansion was made in the subsection (ii) of section 3.4) and given by (3.4.10) for $|k| = \sqrt{2|\delta|} \ll |V_1| \neq 0$. Under the same condition for k and V_1 , $B(k)$ is given by (3.4.9) in its fourth-order power expansion in k . The expansion of $b(k, 1)$ may be simply performed without any complicated condition except for the smallness of k , and given by (app. 1.8). Now one may substitute (3.4.10), (3.4.9), and (app. 1.8) for $\dot{F}(k, r)$, $B(k)$, and $b(k, 1)$, respectively, into (4.2.2):

$$\eta_{\pm}^{\text{pot}}(\gamma) \approx \frac{2\pi}{15\sigma^3} (T_* \tau n^2) \operatorname{Re} \left[\begin{Bmatrix} 1 \\ -i \end{Bmatrix} g_0^{1/2}(1^+) \left\{ -b_0(1) - b_2(1) k^2 - b_4(1) k^4 - \right. \right. \\ \left. \left. - 2 B_0(1 + B_2 k^2 + B_4 k^4) \right\} \right] + \\ + \frac{2\pi}{15\sigma^3} (\tau n^2) \operatorname{Re} \left[\begin{Bmatrix} -i \\ -1 \end{Bmatrix} \langle i F_0(r) + i F_2(r) k^2 + i F_4(r) k^4 \rangle_c \right] .$$

Since all the expansion coefficients are real and $k = \exp(i\pi/4) \cdot \sqrt{2\tau|\gamma_T|}$, one obtains for each component of viscosity coefficients in the leading-term expression:

$$\eta_+^{\text{pot}}(\gamma) \approx \frac{2\pi}{15\sigma^3} (T_* \tau n^2) \left[\left\{ T_*^{-1} \langle F_0(r) \rangle_c - g_0^{1/2}(1^+) (b_0(1) + 2 B_0) \right\} - \right. \\ \left. - \left\{ T_*^{-1} \langle F_4(r) \rangle_c - g_0^{1/2}(1^+) (b_4(1) + 2 B_0 B_4) \right\} (2\tau\gamma_T)^2 \right] \quad (4.2.5A)$$

and

$$\eta_-^{\text{pot}}(\gamma) \approx \frac{2\pi}{15\sigma^3} (T_* \tau n^2) (2\tau\gamma_T) \left[-g_0^{1/2}(1^+) (b_2(1) + 2 B_0 B_2) + T_*^{-1} \langle F_2(r) \rangle_c \right] \quad (4.2.5B)$$

for $|k| = \sqrt{2\tau|\gamma_T|} \ll |k| \neq 0$,

where $\gamma_T = \gamma/2$, and the expansion coefficients are given in the app. 1) and the subsection (ii) of 3.4).

One can rewrite (4.2.5A), the coefficient of shear viscosity, more compactly by introducing the Newtonian viscosity given by

$$\eta_+^{\text{pot}}(0) = \frac{2\pi}{15\sigma^3} (T_* \tau n^2) \left[T_*^{-1} \langle F_0(r) \rangle_c - g_0^{1/2}(1^+) (b_0(1) + 2 B_0) \right] \\ = \frac{4\pi}{15\sigma^3} (T_* \tau n^2) \left(g_0^{1/2}(1^+) / \Delta w_1 + (2T_*)^{-1} \langle F_0(r) \rangle_c \right) \text{ from (app.1.7,8)} \quad (4.2.6)$$

and Eq.(3.4.9), as follows:

$$\eta_+^{\text{pot}}(\gamma) \approx \eta_+^{\text{pot}}(0) \left[1 - A_2 (\tau\gamma)^2 \right] \quad (4.2.7)$$

with

$$A_2 = \left\{ \frac{2\pi}{15\sigma^3} (T_* \tau n^2) / \eta_+^{\text{pot}}(0) \right\} \left\{ T_*^{-1} \langle F_4(x) \rangle_G - g_0^{1/2}(1^+) (b_4(1) + 2 B_0 B_4) \right\}, \quad (4.2.7A)$$

where the relation $\gamma_T = \gamma/2$ has been used.

Intuitively it may be said that the shear pressure is always against (has the opposite sign of) the shear strain, whereas the sign of the normal pressure difference $p_+^{\text{pot}}(\gamma)$ is independent of that of the shear strain in the Couette-flow given by (2.2.7). Accordingly the shear viscosity which is the negative value of the shear pressure divided by the shear rate should be positive, whereas the viscosity of normal pressure difference $\eta_+^{\text{pot}}(\gamma)$ can have either sign but should change its sign when the direction of shear flow is reversed. The positive property of shear viscosity may be explained more rigorously by the entropy production which includes the shear pressure in a shear flow [HIR]. The normal pressure difference doesn't appear in the entropy production and may have either sign [HES3, HIR]. In fact the shear viscosity $\eta_+^{\text{pot}}(\gamma)$ will be proved to be positive for the hard-sphere fluid in the section 4.4). The viscosity of normal pressure difference given by (4.2.5B) changes its sign with the reversed sign of shear rate.

As mentioned before in the subsection (ii) of section 3.4), the inverse correlation length is not absolutely zero even near the liquid-gas phase transition, which implies that $v_1 \neq 0$ for all l , and one may take an arbitrarily small nonzero value of $|k| = \sqrt{\tau|\gamma|}$ under the condition $|k| \ll |v_1| \neq 0$. Therefore the expression (4.2.5) may be said to be the "ultimate" limiting feature of shear viscosity, which includes the second-order term in γ as the leading term. In the appearance of the second-order leading term this limiting shear viscosity agrees with the results by H. Eyring [EVR], B.C. Eu [EU], and S. Hess [HES3].

The linear term in shear rate doesn't appear in the shear viscosity, whereas the viscosity of normal pressure difference given by (4.2.5B) is in proportion to shear rate.

(ii) Shear-rate dependence of the viscosity coefficients for the small shear rate ($|k| < 1$) but much larger than the inverse correlation length

As the limiting feature of deviation factor for small shear rate is determined not by the shear rate alone but by both the shear rate and the inverse correlation length in the two subsections (ii) and (iii) of section 3.4), the limiting feature of viscosity coefficients for small shear rate is determined by the ratio of the shear rate to the inverse correlation length, $|k/v_1| = \sqrt{\tau|\tau|}/|v_1|$. The last subsection corresponds to the values of $|k/v_1| \ll 1$ and this subsection deals with the condition: $|k/v_1| \gg 1$ and $|k| < 1$. In order to have the values of $|k|$ much larger than the inverse correlation length but still quite smaller than unity the inverse correlation length (or correlation length) itself should be very small (or very large). This implies that the fluid system is near liquid-gas phase transition. Therefore the fluid system considered here is assumed to be in the vicinity of such a phase transition that the inverse correlation length becomes very small and there exists at least one of the $|v_1|$'s much smaller than $|k| (< 1)$. Similarly to the subsection (iii) of section 3.4) it suffices to consider the second-order approximation for equilibrium density correlation function denoted by (3.4.13), in which only one complex-conjugate pair of the v_1 's appears and $|v_1| \ll |k|$ for all l in this situation.

All the procedures are similar to those made in the last subsection except for replacing $B(k)$ and $\hat{F}(k, r)$ by their limiting forms given by (3.4.17) and (3.4.18), respectively in the expression (4.2.2) for viscosity coefficients. Then one has

$$\begin{aligned} \eta_+^{\text{pot}}(\tau) \approx & \frac{2\pi}{15\sigma^3} (\tau_* \tau n^2) \cdot \text{Re} \left[\begin{Bmatrix} 1 \\ -i \end{Bmatrix} g_0^{1/2}(1^+) \left\{ -b_0(1) - b_2(1) k^2 - \right. \right. \\ & \left. \left. - 2 B_0^{\zeta} (1 + i B_1^{\zeta} k) \right\} \right] + \\ & + \frac{2\pi}{15\sigma^3} (\tau n^2) \cdot \text{Re} \left[\begin{Bmatrix} -i \\ -1 \end{Bmatrix} \langle i F_0^{\zeta}(r) + F_1^{\zeta}(r) k \rangle_c \right] , \end{aligned}$$

where the power expansion of $b(k,1)$ is substituted from (app. 1.8) and the range of integration in the second term is cut off according to (4.2.3). Since all the expansion coefficients are real and $k \approx \exp(i\pi/4) \cdot \sqrt{2\tau|\gamma|}/r$, one obtains for each component of viscosity coefficients in the leading-term expression:

$$\eta_+^{\text{pot}}(\gamma) \approx \frac{2\pi}{15\sigma^3} (T_* \tau n^2) \left[\left\{ T_*^{-1} \langle F_0^<(\mathbf{r}) \rangle_c - g_0^{1/2}(1^+) (b_0(1) + 2 \theta_0^<) \right\} + \left\{ T_*^{-1} \langle F_1^<(\mathbf{r}) \rangle_c + 2 g_0^{1/2}(1^+) \theta_0^< \theta_1^< \right\} \sqrt{2\tau|\gamma|} \right] \quad (4.2.8A)$$

and

$$\eta_-^{\text{pot}}(\gamma) \approx \frac{2\pi}{15\sigma^3} (T_* \tau n^2) (\sqrt{2\tau|\gamma|}) \left[-T_*^{-1} \langle F_1^<(\mathbf{r}) \rangle_c - 2 g_0^{1/2}(1^+) \theta_0^< \theta_1^< \right] \quad (4.2.8B)$$

for $|\gamma| \ll |k| < 1$,

where $\gamma_r = \gamma/2$, and η_-^{pot} should change its sign with the reversed sign of γ . The sign is hidden in (4.2.8B) because of the assumption, $\gamma > 0$. One may rewrite (4.2.8A) more compactly as follows:

$$\eta_+^{\text{pot}}(\gamma) \approx \eta_+^< \left\{ 1 - A_{1/2}^<(\tau|\gamma|)^{1/2} \right\} \quad (4.2.9)$$

with

$$\eta_+^< \equiv \frac{2\pi}{15\sigma^3} (T_* \tau n^2) \left[T_*^{-1} \langle F_0^<(\mathbf{r}) \rangle_c - g_0^{1/2}(1^+) (b_0(1) + 2 \theta_0^<) \right] \quad (4.2.10A)$$

$$A_{1/2}^< \equiv \left[\frac{\sqrt{2}\pi}{15\sigma^3} (T_* \tau n^2) / \eta_+^< \right] \cdot \left[-T_*^{-1} \langle F_1^<(\mathbf{r}) \rangle_c - 2 g_0^{1/2}(1^+) \theta_0^< \theta_1^< \right] \quad (4.2.10B)$$

where the relation $\gamma_r = \gamma/2$ has been used, and "<" means the condition (3.4.14): $|\gamma| \ll |k| < 1$ for all l .

It should be noticed that the expression (4.2.9) is asymptotic and $\eta_+^<$ is not the Newtonian viscosity. One may not take the zero value of shear rate in (4.2.9), since the shear rate is confined to the condition: $0 < |\dot{\gamma}_1| \ll |k| = \sqrt{\tau/\eta} < 1$. The value of $\eta_+^<$ departs slightly from the Newtonian viscosity $\eta_+^{\text{pot}}(0)$ given by (4.2.6). This error consists of such terms like $(\dot{\gamma}_1/k)^n$ multiplied by $\dot{\gamma}_1^m k^n$ ($m = 2, 3, 4$ and $n = 0, 1, 2 \dots$) and is about in the order of $\dot{\gamma}_1^2$. The factors $(\dot{\gamma}_1/k)^n$ for n integer arise from the power expansion (3.4.15) of the rational function $(ik + \dot{\gamma}_1)^{-n}$ with respect to $(\dot{\gamma}_1/k)$.

Since the repulsive part of the Lennard-Jones-like potential is replaced by the effective hard wall in (3.1.1), the behavior of $g_0(r)$ at $r = 1^+$ is expected to be significantly different from that of the original L-J-like fluid at $r = 1$, where $r = 1$ is not the position of zero point of the L-J potential but the unit of length in the diameter of effective hard sphere which depends upon both temperature and density, and is determined by the equation (3.1.2). The calculation of the effective hard-sphere diameter σ is suggested by L. Verlet and J.J. Weiss [V-W]. In general the effective hard-sphere diameter becomes smaller as the temperature or the density increases [AND]. It is expected that for high temperatures and densities $g_0(r)$ just near the hard core behaves like $g_{0\sigma}(r)$, the equilibrium pair-correlation function for hard spheres.

Although the ansatz (3.1.1) for intermolecular potential is somewhat different from the original L-J-like potential, the fluid system of molecules with the potential (3.1.1) may well be expected to show the true behavior of the original fluid system. Thus it is of great interest to know the values of $\eta_+^<$ and $A_{1/2}^<$ near a liquid-gas phase transition, and compare them with the results from experiments.

Recently some workers [EVA, EHH] showed such a nonanalytic behavior of shear viscosity coefficient of the Lennard-Jones fluid at the triple point, it is not yet clear whether the inverse correlation length at the triple point is so small that one may observe the nonanalytic behavior (4.2.9) in quite a wide range of the shear rate. If one observes a large value of compressibility at the triple point (i.e. a small value of inverse correlation length), the expression (4.2.9) is correct there restricted to the range: $|v_1| \ll |k| = \sqrt{\tau\gamma} < 1$. The prediction (4.2.9) is essentially different from that of Kawasaki [KAW] especially in describing its valid range of shear rate.

For the hard-sphere fluid the nonanalytic behavior (4.2.9) may be hardly observed, for it doesn't undergo the gas-liquid-like phase transition, i.e. the pair-correlation function of hard spheres is not of long range and there happens no clustering of hard spheres.

(iii) Shear-rate dependence of the viscosity coefficients in the large shear rate limit

The limiting functional form of $\overset{\circ}{F}(k, r)$ is calculated in the subsection (iv) of section 3.4 and given by (3.4.22). The limiting features of $b(k, 1)$ and $B(k, 1)$ in (4.2.2) may be easily deduced by using their more explicit expressions (4.1.10) and (3.3.29D), respectively:

$$b(k, 1) = -6 (2 + s_1) (1 - i k - \frac{1}{3} k^2) / Q(k) \quad \text{from (4.1.10)}$$

$$= \left\{ -6 (2 + s_1) / Q_0 \right\} (1 - i k - \frac{1}{3} k^2) / (1 - i k + Q_2 k^2 + i Q_3 k^3) \quad \text{from (3.3.29D)}$$

$$\sim \left\{ -6 (2 + s_1) / Q_0 \right\} \left\{ -\frac{1}{3} / (i Q_3 k) \right\} \quad \text{for large } |k| .$$

Since $Q_0 Q_3 = 2$ from (3.3.29D) and $k = e^{i\pi/4} \sqrt{\tau|\gamma|}$, one has

$$b(k, 1) \sim -\frac{1}{\sqrt{2}} (1 + i) (2 + s_1) (\tau|\gamma|)^{-1/2} \quad \text{for large } \gamma . \quad (4.2.11)$$

From (3.3.29D) $B(k)$ is represented as follows

$$\begin{aligned} B(k) &= N(k) / Q(k) \\ &= \left[\sum_1^{\#} u_1 \left\{ 3 - v_1(3 + v_1) - i k (1 - v_1) + \frac{v_1^2 (4 + v_1)}{v_1 + i k} - \right. \right. \\ &\quad \left. \left. - \frac{v_1^3}{(v_1 + i k)^2} \right\} \right] \cdot Q_0^{-1} \cdot \left[1 - i k + Q_2 k^2 + i Q_3 k^3 \right] \end{aligned}$$

As $|k| \rightarrow \infty$, it becomes

$$B(k) \sim \left\{ \sum_1^{\#} u_1 (v_1 - 1) \right\} (i k) / (i Q_0 Q_3 k^3)$$

or

$$B(k) \sim -\frac{i}{2} g_0'(1^+) / (\tau|\gamma|) , \quad (4.2.12)$$

where the relations

$$\sum_1^{\#} u_1 (v_1 - 1) \cong \left\{ \frac{d}{dr} s(r) \right\}_{r=1^+} = \left\{ \frac{d}{dr} g_0(r) \right\}_{r=1^+} \equiv g_0'(1^+)$$

and

$$Q_0 Q_3 = 2 \quad \text{from (3.3.29D)}$$

have been used.

Substitution of (4.2.11, 12) and (3.4.22) into (4.2.2) gives

$$\eta_{+}^{\text{pot}}(\gamma) \sim \frac{2\pi}{15\sigma^3} (T_* \tau n^2) \cdot \text{Re} \left[\left\{ \begin{matrix} 1 \\ -i \end{matrix} \right\} g_0^{1/2}(1^+) \left\{ \frac{1+i}{\sqrt{2}} (2 + s_1^+) (\tau|\gamma|)^{-1/2} + i g_0'(1^+)/(\tau|\gamma|) \right\} \right] + \frac{2\pi}{15\sigma^3} (\tau n^2) \cdot \text{Re} \left[\left\{ \begin{matrix} -i \\ -1 \end{matrix} \right\} \langle r g_0'(r)/(\tau|\gamma|) \rangle \right].$$

Finally one obtains for each component, neglecting the terms in proportion to $1/\gamma$,

$$\eta_{+}^{\text{pot}}(\gamma) \sim \frac{\sqrt{2}}{15\sigma^3} \pi (T_* \tau n^2) g_0^{1/2}(1^+) (g_0(1^+) + 1) (\tau|\gamma|)^{-1/2} \quad (4.2.13A)$$

for large γ ,

$$\eta_{-}^{\text{pot}}(\gamma) \sim \frac{\sqrt{2}}{15\sigma^3} \pi (T_* \tau n^2) g_0^{1/2}(1^+) (g_0(1^+) + 1) (\tau|\gamma|)^{-1/2} \quad (4.2.13B)$$

where s_1^+ has been replaced by $g_0(1^+) - 1$.

As one can see in (4.2.13A, B), for large shear rate the viscosity coefficients of shear pressure and normal pressure difference in x- and y-direction have the similar functional form except for the sign. The shear viscosity and the viscosity of normal-pressure difference decrease quite slowly in the minus half-power order for large shear rate. This implies at the same time that the shear pressure and the normal pressure difference increase slowly in the plus half-power order for large shear rate:

$$\begin{aligned} p_{+}^{\text{pot}}(\gamma) &= -\eta_{+}^{\text{pot}}(\gamma) \cdot \gamma \\ &\sim -\frac{\sqrt{2}}{15\sigma^3} \pi (T_* \tau n^2) g_0^{1/2}(1^+) (g_0(1^+) + 1) (\tau|\gamma|)^{1/2} \end{aligned} \quad (4.2.14A)$$

and

$$\begin{aligned} p_{-}^{\text{pot}}(\gamma) &= -\eta_{-}^{\text{pot}}(\gamma) \cdot \gamma \\ &\sim \frac{\sqrt{2}}{15\sigma^3} \pi (T_* \tau n^2) g_0^{1/2}(1^+) (g_0(1^+) + 1) (\tau|\gamma|)^{1/2} \end{aligned} \quad (4.2.14B)$$

Here one has the negative normal-pressure difference in the large shear rate limit, which implies that $p_{xx}^{\text{pot}} < p_{yy}^{\text{pot}}$. The shear pressure works against the shear strain in (4.2.14A).

4.3) The fluid-to-solid-like phase transition

In this section some exotic behaviors of the viscosity coefficients will be shown at the fluid-solid phase transition especially in the zero shear rate limit. One can observe these exotic behaviors in the viscosity coefficients obtained in section 4.1) and given by (4.2.2). The condition for this fluid-to-solid-like phase transition will be given for the fluid system of molecules with the intermolecular potential (3.1.1). The density at fluid-to-solid-like phase transition for the hard spheres will be calculated.

(i) An equation of condition for the fluid-to-solid-like phase transition

In obtaining the power series of the function $b(k,r)$ one had first to expand $1/C_+^{(1)}$ in (App.1.7) under the assumption (App. 1.7A):

$$w_1 := (2T_*)^{-1} w^*(1^+) \text{ defined by (App.1.6)}$$

$$\dagger 3.$$

When $w_1=3$, the power expansion (App.1.7) is not valid. In this situation one should return to the original expression for viscosity coefficients (4.1.8). The main part of this expression is the function $F(k,r)$, which may be rewritten here as

$$F(k,r) \approx \overset{\circ}{F}(k,r) = ip(k,r) + ib(k,r) + iq(k,r)B(k) \text{ from (3.4.5)}$$

$$\overset{\circ}{F}(k,1) = ib(k,1) + i2B(k) \text{ with } p(k,1)=0 \text{ and } q(k,1)=2$$

$$\text{from (4.1.11).}$$

As one can see in (3.4.5), the two functions $p(k,r)$ and $q(k,r)$ do not contain any rational function of k and r and be-

have normally. But $b(k,r)$ and $B(k)$ are rational functions with the common denominator $C_+^{(1)}$ which consists in w_1 and the spherical Hankel function of first kind, and is defined by (3.3.23 and 13B). The two functions $b(k,r)$ and $B(k)$ with the multiplying factor $q(k,r)$ may be written explicitly by using the expressions (4.1.10) and (3.3.29D) as follows:

$$b(k,r)+q(k,r)B(k) = \left(-6(1+\delta_{1,r}) (1+s_1^>/2) r^{-3} e^{ik(r-1)} (1-ikr-k^2 r^2/3) + q(k,r)N(k) \right) / \left(6(3-w_1) (1-ik) + 2(w_1-4)k^2 + i2k^3 \right), \quad (4.3.1)$$

where $N(k)$ is defined in (3.3.29D).

Now one substitutes the following special value for w_1

$$w_1 := (2T_*)^{-1} w'(1^+) = 3 \quad (4.3.2)$$

into (4.3.1) and obtains

$$b(k,r)+q(k,r)B(k) = \left(-6(1+\delta_{1,r}) (1+s_1^>/2) r^{-3} e^{ik(r-1)} (1-ikr-k^2 r^2/3) + q(k,r)N(k) \right) / \left(-2k^2 (1-ik) \right). \quad (4.3.3)$$

When one takes the zero shear rate limit, i.e. $|k| \rightarrow 0^+$, in (4.3.3), one obtains the following limiting expression for (4.3.1):

$$b(k,r)+q(k,r)B(k) \approx \left(\{N_0 q_0(r) - 6(1+\delta_{1,r}) (1+s_1^>/2) r^{-3}\} (1-ik) + \{N_0 N_2 q_0(r) + N_0 q_2(r) - (1+\delta_{1,r}) (1+s_1^>/2) r^{-3} (r^2-3)\} \cdot k^2 \right) / \left(-2k^2 (1-ik) \right) \quad (4.3.3A)$$

and

$$b(k,1) + q(k,1)B(k) = b(k,1) + 2B(k)$$

$$\approx \{2\{N_0 - 3(1+\delta_{1,r})(1+s_1^2/2)\}(1-ik) + 2\{N_0 N_2 + (1+\delta_{1,r})(1+s_1^2/2)\}k^2\} / (-2k^2(1-ik)), \quad (4.3.3B)$$

since $q(k,1)=q_0(1)=2$ and $q_2(1)=0$ from (4.1.9) and (App.1.9). The terms in the numerators of (4.3.3A and B) are taken to the second order in k , and $N(k)$ has been calculated from (3.3.29D) as follows

$$N(k) \approx N_0(1 - ik + N_2 k^2)$$

$$\text{with } N_0 = 3 \Sigma_1^\# u_1 = 3\{g_0(1^+) - 1\}$$

$$N_2 = -3^{-1} - (2/N_0) \Sigma_1^\# u_1 / v_1. \quad (4.3.4)$$

The expansion of the rational function $N(k)$ is valid, for the v_1 's do never vanish, as mentioned before, and k may be taken arbitrarily small so that $|k/v_1| \ll 1$.

On substituting $\bar{F}(k,r)$ and $\bar{F}(k,1)$ with the limiting forms of $b(k,r)+q(k,r)B(k)$ and $p(k,r)$ given by (4.3.3A,B) and (App.1.5), respectively, into the expression (4.2.2) for viscosity coefficients, one has

$$\begin{aligned} \eta_{\pm}^{\text{pot}}(\gamma) \approx & \frac{2\pi}{15} (T_* \tau n^2 / \sigma^3) \text{Re} \left[\left\{ \begin{matrix} 1 \\ -i \end{matrix} \right\} g_0^{1/2}(1^+) \{ (N_0 - 6 - 3s_1^2) k^{-2} + \right. \\ & \left. + (N_0 N_2 + 2 + s_1^2)(1 + ik) \} \right] + \\ & + \frac{2\pi}{15} (\tau n^2 / \sigma^3) \text{Re} \left[\left\{ \begin{matrix} 1 \\ -i \end{matrix} \right\} \left\langle \left\{ -\frac{N_0}{2} q_{b_0}(r) + 3(1+\delta_{1,r})(1+\frac{s_1^2}{2})r^{-3} \right\} k^{-2} + \right. \right. \\ & + p_0(r) + \left\{ -\frac{N_0 N_2}{2} q_{b_0}(r) - \frac{N_0}{2} q_{b_2}(r) + \right. \\ & \left. \left. + \frac{1}{2}(1+\delta_{1,r})(1+\frac{s_1^2}{2})(r^2-3)r^{-3} \right\} (1+ik) \right\rangle \right], \end{aligned}$$

where the terms are taken to the first order of k for small k , and $g_0(r)$ is independent of density and temperature, as can be seen in App.1. The integration $\langle \dots \rangle_c$ is defined by

$$\langle \dots \rangle_c = \int_{r_m}^{\infty} r^3 v_a(r) g_0^{1/2}(r) \{ \dots \} dr, \quad (4.3.5)$$

where $g_0(r)$ satisfies the condition (4.3.2), which will be discussed later.

Since $k = e^{i\pi/4} (\tau|\gamma|)^{1/2}$, one obtains for each component of viscosity coefficients: for $w_1 = 3$

$$\begin{aligned} {}^* \eta_+^{\text{pot}}(\gamma) \approx & \frac{2\pi}{15} (T_* n^2 \tau / \sigma^3) g_0^{1/2}(\gamma) \{ N_0 N_2 + 2 + S_1^2 \} \{ 1 - \sqrt{\tau|\gamma|/2} \} + \\ & + \frac{2\pi}{15} (n^2 \tau / \sigma^3) \left[\langle p_0(r) \rangle_c + \left\langle -\frac{1}{2} N_0 N_2 q_{10}(r) - \frac{1}{2} N_0 q_{12}(r) + \right. \right. \\ & \left. \left. + \frac{1}{4} (2 + S_1^2) (r^2 - 3) / r^3 \right\rangle_c \cdot \{ 1 - \sqrt{\tau|\gamma|/2} \} \right] \end{aligned} \quad (4.3.6A)$$

and

$$\begin{aligned} {}^* \eta_-^{\text{pot}}(\gamma) \approx & \frac{2\pi}{15} (T_* n^2 \tau / \sigma^3) (\tau \gamma)^{-1} \left[g_0^{1/2}(\gamma) \{ -N_0 + 6 + 3S_1^2 \} + \right. \\ & \left. + T_*^{-1} \left\langle \frac{1}{2} N_0 q_{10}(r) - 3(1 + S_1^2/2) / r^3 \right\rangle_c \right] + \frac{\pi}{15} (T_* n^2 \tau / \sigma^3) \sqrt{2\tau|\gamma|} \cdot \\ & \cdot \left[(N_0 N_2 + 2 + S_1^2) + (2T_*)^{-1} \left\langle -N_0 N_2 q_{10}(r) - N_0 q_{12}(r) + (1 + \frac{S_1^2}{2}) (r^2 - 3) / r^3 \right\rangle_c \right], \end{aligned} \quad (4.3.6B)$$

where N_0 and N_2 are given by (4.3.4), and the stars in ${}^* \eta_{\pm}^{\text{pot}}$ denote the condition " $w_1 = 3$ ".

One finds here a very interesting phenomenon: when $w_1 = 3$, the viscosity coefficient of normal-pressure difference diverges in the zero shear rate limit! The shear viscosity coefficient (4.3.5A) seems to be normal except for having the nonanalytic square-root- γ term. But it should be noticed that the shear viscosity ${}^* \eta_+^{\text{pot}}(0)$ obtained from (4.3.6A) is somewhat different

from the Newtonian viscosity given by (4.2.6). For $\gamma=0$ the shear viscosity of (4.3.6A) becomes

$$\begin{aligned} \eta_+^{\text{pot}}(0) := & \frac{\pi}{15} (\tau_* \tau \pi^2 / \sigma^3) \left[4 \sqrt{q_0(1^+)} \left(1 - \sum_{\ell}^{\#} \nu_{\ell} / \nu_{\ell} \right) + \frac{2}{\tau_*} \langle p_0(r) \rangle_c - \right. \\ & \left. - \tau_*^{-1} \langle N_0 N_2 q_0(r) + N_0 q_{b2}(r) - (1 + \frac{S_1}{2})(r^2 - 3)r^{-3} \rangle_c \right] \quad (4.3.7) \end{aligned}$$

for $w_1=3$, where N_0 and N_2 are replaced in the first term by their values given by (4.3.4).

To deduce the physical meaning of this exotic phenomenon we consider the pressure tensor. The pressure components corresponding to (4.3.6A and B) respectively, are

$$P_+^{\text{pot}}(\gamma) \cong - \eta_+^{\text{pot}}(0) \cdot \gamma \rightarrow 0 \quad \text{as } \gamma \rightarrow 0 \quad (4.3.8A)$$

and

$$\begin{aligned} P_-^{\text{pot}}(\gamma) \rightarrow P_-^{\text{pot}}(0^+) := & - \frac{\pi}{15} (\tau_* \pi^2 / \sigma^3) \left[2 \sqrt{q_0(1^+)} (6 + 3 S_1^{\rightarrow} - N_0) + \right. \\ & \left. + \tau_*^{-1} \langle N_0 q_{b0}(r) - 3(2 + S_1^{\rightarrow}) r^{-3} \rangle_c \right] \quad \text{as } |\gamma| \rightarrow 0^+, \quad (4.3.8B) \end{aligned}$$

where $\eta_+^{\text{pot}}(0)$ is defined by (4.3.7), and 0^+ is to be understood as an infinitesimally small positive but nonzero number.

The shear pressure vanishes at the zero shear rate limit, which is normal. But the normal pressure difference has nonzero value in the zero shear rate limit, which cannot immediately be understood. At the zero shear rate, i.e. in equilibrium the pressure is isotropic and there occur no normal pressure differences. But it is the matter of thinking about the order of physical occurrences: at the zero shear rate, in fact, there are no pressure differences. In this equilibrium state, however, one cannot observe any kind of nonequilibrium phenomena. In order to see something in nonequilibrium one had to assume the nonzero value of shear rate γ and performed the perturbation expansion in $\gamma_d = \gamma/2$. Thus one should understand the

result (4.3.8B) in the sense of infinitesimally small but non-zero shear rate. Mathematically speaking, the limiting process $w_1 \rightarrow 3$ and $\gamma \rightarrow 0$ may not be interchanged to obtain the nonzero value of $*p_-^{\text{pot}}(0^+)$. The normal pressure difference at $w_1=3$ jumps from its zero value at the zero shear rate to a finite value discontinuously as soon as the shear flow has been "switched on". Thus one can rewrite the zero-limit values of normal pressure difference as follows:

$$\lim_{\gamma \rightarrow 0^+} p_-^{\text{pot}}(\gamma) = \begin{cases} 0, & w_1 < 3 \text{ from (4.2.5B)} \\ *p_-^{\text{pot}}(0^+) \neq 0, & w_1 = 3 \text{ from (4.3.8B)}. \end{cases} \quad (4.3.9)$$

The Newtonian shear viscosity coefficient diverges as $(3-w_1) \rightarrow 0^+$:

$$\lim_{\gamma \rightarrow 0^+} \eta_+^{\text{pot}}(\gamma) = \begin{cases} \eta_+^{\text{pot}}(0) \rightarrow \infty \text{ as } (3-w_1) \rightarrow 0^+ \text{ from (4.2.6)} \\ \quad \text{or (4.1.12)'} \\ \eta_+^{\text{pot}}(0): \text{ finite at } w_1=3 \text{ from (4.3.7)}. \end{cases} \quad (4.3.10)$$

The Newtonian shear viscosity given by (4.2.6) includes the terms proportional to $b_0(1)$ and B_0 which are given in (App.1.8) and (3.4.9), respectively. These two expansion coefficients have their common factor $C_0^{(1)} := 1/(3-w_1)$ which is given also in (App.1.7) and diverge as $(3-w_1) \rightarrow 0^+$. Thus the Newtonian shear viscosity given by (4.2.6) has very large values near $w_1=3$ and becomes still larger without limit as the value of w_1 approaches to 3. This constitutes a very sharp peak of the shear viscosity coefficient at $\gamma=0$ near $w_1=3$. This will be discussed in the next subsection.

The jump of the normal press. difference and the divergence of the Newtonian shear viscosity coefficient at "switching on" the shear flow are here interpreted as a fluid-to-solid-like phase transition. The condition for this phase transition was

given by (4.3.2), which may be here written more explicitly:

$$\begin{aligned} 3 = w_1 &= (2T_*)^{-1} w'(1^+) \text{ from (App.1.6)} \\ &= -2^{-1} \{d/dr \ln g_0(r)\}_{r=1^+} \text{ from (2.2.1) and (2.1.19)} \end{aligned}$$

or

$$6g_0(1^+) + g'_0(1^+) = 0. \quad (4.3.11)$$

The condition (4.3.11) is a relation between density and temperature, and responsible for the exotic behaviors (4.3.9) and (4.3.10) or the fluid-to-solid-like phase transition. Thus the equation (4.3.11) depicts the temperature-density line at the fluid-to-solid-like phase transition of the fluid system of molecules with the intermolecular potential (3.1.1).

In deriving the condition (4.3.11) one has nothing to do with the approximations which were introduced to calculate the deviation factor x_1^0 and the viscosity coefficients. It is related to the position of the singularity of the viscosity coefficients which is independent of the approximations introduced. Here, the ansatz for intermolecular potential (3.1.1) again plays the most important role in obtaining the condition (4.3.11).

Since the P-Y^{HS} equation is solved exactly /WER,THI/ and given by (3.2.14), one may now check the condition (4.3.11):

$$\begin{aligned} g_\sigma(1^+) &= y_\sigma^<(1) \text{ for hard spheres} \\ &= (1 + x/2)/(1 - x)^2 \text{ from (3.2.14),} \end{aligned} \quad (4.3.12A)$$

and

$$\begin{aligned} g'_\sigma(1^+) &= \{d/dr y_\sigma^<(r)\}_{r=1} \text{ for hard spheres} \\ &= -(9x/2)(1 + x)/(1 - x)^3 \text{ from (3.2.14).} \end{aligned} \quad (4.3.12B)$$

Substitution of (4.3.12A,B) into the condition (4.3.11) gives the following equation for the transition density:

$$6(1+x/2)/(1-x)^2 - (9x/2)(1+x)/(1-x)^3 = 0$$

or

$$5x^2 + 5x - 4 = 0.$$

The positive solution of this algebraic equation is

$$\begin{aligned} x^* &= (1.05)^{1/2} - 0.5 \\ &= 0.524695 \dots \end{aligned} \quad (4.3.13)$$

Since the P-Y equation itself is not correct, some deviation from experiments is expected to be found in (4.3.13). But the value of x^* in (4.3.13) doesn't depart so away from the experimental data about the transition density for HS /A-W/, $x_{tr} \sim 0.48$. Recently L. Verlet and J.J. Weis improved the P-Y equilibrium pair-correlation function for hard spheres /V-W/. This improvement for $y_0(r)$ may be introduced to correct the value of x^* in (4.3.13).

The switching-on value of normal pressure difference at the fluid-to-solid-like phase transition for hard spheres may be easily obtained from (4.3.8B). The second term of soft-part contribution vanishes identically in (4.3.8B) for hard spheres and one obtains

$$\begin{aligned} HS^* p_{-}^{pot}(0^+) &= -(4\pi/5) (T_* n^2 / \sigma^3) g_0^{1/2}(1^+) \\ &= -(28.8/\pi) (T_* x^{*2} / \sigma^3) g_0^{1/2}(1^+) \text{ for HS,} \end{aligned} \quad (4.3.14)$$

where $s_1^>$ and N_0 have been replaced by the values given in (3.3.30C) and (4.3.4), respectively, and $g_0(1^+)$ satisfies the condition (4.3.11).

Since $g_0(1^+)$ is always positive, the switching-on value $HS_{p_{xx}}^{\text{pot}}(0^+)$ at the transition is negative, which implies

$$HS_{p_{xx}}^{\text{pot}}(0^+) < HS_{p_{yy}}^{\text{pot}}(0^+).$$

The switching-on shear viscosity coefficient for HS at the transition may also be obtained from (4.3.7) by replacing N_0 and N_2 by their expressions in (4.3.4):

$$HS_{*} \eta_{+}^{\text{pot}}(0) = \frac{4\pi}{15} (\tau_* n^2 \tau / \sigma^3) g_0^{1/2}(1^+) \left\{ 1 - \sum_{\ell}^{\#} u_{\ell} / v_{\ell} \right\}. \quad (4.3.15)$$

$$\text{Since } - \sum_{\ell}^{\#} u_{\ell} / v_{\ell} = \int_1^{\infty} \sum_{\ell}^{\#} u_{\ell} e^{\frac{1}{2}(r-1)} dr \cong \int_1^{\infty} r s^{\sim}(r) dr,$$

one has an alternative approximate representation:

$$HS_{*} \eta_{+}^{\text{pot}}(0) = \frac{4\pi}{15} (\tau_* n^2 \tau / \sigma^3) g_0^{1/2}(1^+) \left\{ 1 + \int_1^{\infty} (g_0(r) - 1) dr \right\}, \quad (4.3.15)'$$

where $s^{\sim}(r) = g_0(r) - 1$.

Here some remarks should be added to the transition condition (4.3.11). The origin of this condition is the secondary boundary condition for the soft force contribution to the radial component of the excess probability current density, which is given by (3.3.13A): $\lim_{r \rightarrow 1+} j_r^S(r, \theta, \phi) = 0$. The physical meaning of this secondary boundary condition is the absence of the soft force contribution to the radial component of excess probability current at the hard core in the relative pair space, which was explained in detail in the section 3.3). The condition (4.3.11) is related to the definite value of the mean force at the hard core in the relative pair space, which was approximated in (2.1.18) by its equilibrium value as follows

$$\begin{aligned} \underline{F} &\cong \underline{F}^{\text{eq}} = -\nabla_w \\ &= T_* \underline{\hat{r}} g_0'(r) / g_0(r), \end{aligned}$$

where $\underline{\hat{r}}$ is the radial vector with unit length.

But this approximation becomes exact in the zero shear-rate limit, as mentioned before. Since any other kind of approximation has not been introduced for the condition (4.3.11), as already mentioned, it is expected to predict quite correct values of density and temperature at which "the fluid-to-solid-like phase transition" occurs in the fluid system of molecules with the potential type (3.1.1) in the zero shear-rate limit. The intermolecular potential (3.1.1) was simply introduced as an ansatz. But it may be so chosen that the "correct" value of Helmholtz free energy may be obtained. Thus the fluid system of molecules with the potential (3.1.1) is not far away from the L-J-like fluid system and moreover expected to show us some features similar to those of the realistic fluid system.

Another remark is the following: One knows that the $P-Y^{HS}$ equation shows no fluid-to-solid-like phase transition. Nevertheless the solution of the $P-Y^{HS}$ equation was introduced to solve the equation (4.3.11) for the transition density x^* . This seems to be somewhat paradoxical. Now one considers the physical meaning of the fluid-to-solid phase transition. In equilibrium theory the fluid-to-solid phase transition may be observed by the response to the compression and the compressibility is expected to have a sudden large value at the beginning of transition because of the arrangement of the molecules. But here in the nonequilibrium theory one observes the response to the shear strain and the viscosity coefficients are expected to show some exotic behavior at the beginning of the fluid-to-solid phase transition: here, for example, the divergence of the Newtonian viscosity, which may be intuitively understood to be caused by the tendency of becoming tough of the liquid. Thus the experimental mechanism is different from each other and the paradox doesn't seem to be so serious.

(ii) The behaviors of the viscosity coefficients near the
fluid-to-solid-like phase transition

Instead of the value $w_1 = 3$ one may take the value of w_1 near 3 as follows

$$0 < (3 - w_1) =: \Delta w_1 \ll 1. \quad (4.3.16)$$

Then the expression (4.3.1) may be rewritten in the following way

$$b(k, r) + q(k, r)B(k) = \left[-6(1 + \delta_{1,r})(1 + s_1/2)r^{-3}e^{ik(r-1)}(1 - ikr - \frac{k^2 r^2}{3}) + \right. \\ \left. + q(k, r)N(k) \right] / \left[\{6\Delta w_1(1 - ik) - 2\Delta w_1 k^2\} - \right. \\ \left. - 2(1 - ik)k^2 \right]. \quad (4.3.17)$$

Since $\Delta w_1 \ll 1$, the first term in the denominator of (4.3.17) may be neglected for $|k| > 1$. But the negligence of this term for the range $0 < |k| < 1$ requires some criterion. To examine this criterion it is sufficient to consider $b(k, 1) + q(k, 1)B(k)$, which is the main contribution to the viscosity coefficients. Here one considers the following two situations: a) $1 \gg |\Delta w_1| \ll |k^2| = |\tau\gamma|$ and b) $|\tau\gamma| = |k^2| \ll |\Delta w_1| \ll 1$.

a) $1 \gg |\Delta w_1| \ll |k^2| = |\tau\gamma|$: Nonanalytic behavior

In this situation one may neglect Δw_1 in the expression (4.2.2) for viscosity coefficients as if it were zero. Then one obtains the following approximate representation for the viscosity coefficients from (4.2.2):

$$\eta_{\pm}^{\text{pot}}(\gamma) \cong \frac{2\pi}{15} (\tau_* n^2 \tau / \sigma^3) \text{Re} \left[\begin{Bmatrix} 1 \\ -i \end{Bmatrix} g_0^{1/2}(1^+) \{ -b^*(k, 1) - 2B^*(k) \} \right] + \\ + \frac{2\pi}{15} (n^2 \tau / \sigma^3) \text{Re} \left[\begin{Bmatrix} -i \\ -1 \end{Bmatrix} \langle F^*(k, r) \rangle_c \right], \quad (4.3.18)$$

where $b^*(k, r) + q^*(k, r) B^*(k)$ is given by (4.3.3) and the superscript "*" means that the temperature and the density in the corresponding quantity with the star as superscript satisfy the transition condition (4.3.11). Notice that the expression above becomes exact at the fluid-to-solid-like phase transition, i.e. $\Delta w_1 = 0$.

The asymptotic feature of (4.3.18) for the range of shear rate $|\Delta w_1| \ll |\tau\gamma| \ll 1$ may be given by (4.3.6A and B) and re-written compactly as follows

$$\eta_+^{\text{pot}}(\gamma) \cong {}^*\eta_+^{\text{pot}}(0) \left\{ 1 - A_{1/2}^{\text{F-S}} (\tau|\gamma|)^{1/2} \right\} \quad (4.3.19A)$$

$$\eta_-^{\text{pot}}(\gamma) \cong -{}^*P_-^{\text{pot}}(0^+) \gamma^{-1} \left\{ 1 + A_{3/2}^{\text{F-S}} (\tau|\gamma|)^{3/2} \right\}, \quad (4.3.19B)$$

where ${}^*\eta_+^{\text{pot}}(0)$ and ${}^*P_-^{\text{pot}}(0^+)$ are the switching-on values of the shear viscosity and the normal pressure difference at the fluid-to-solid phase transition and given by (4.3.7) and (4.3.8B), respectively. The two coefficients $A_{1/2}^{\text{F-S}}$ and $A_{3/2}^{\text{F-S}}$ are defined by

$$A_{1/2}^{\text{F-S}} := \frac{1}{\sqrt{2}} \left\{ 1 - \frac{2\pi}{15} (\tau n^2 / \sigma^3) \langle p_o(r) \rangle_c / {}^*\eta_+^{\text{pot}}(0) \right\} \quad (4.3.19C)$$

and

$$A_{3/2}^{\text{F-S}} := \left\{ \frac{\sqrt{2}\pi}{15} (\tau_* \tau n^2 / \sigma^3) / {}^*P_-^{\text{pot}}(0^+) \right\} \cdot \left\{ (N_0 N_2 + 2 + S_1^2) - \frac{1}{2T_*} \langle N_0 N_2 q_{b_0}(r) + N_0 q_{b_2}(r) - \frac{2+S_1^2}{2r^3} (r^2-3) \rangle_c \right\}. \quad (4.3.19D)$$

In (4.3.19C and D) the superscript "F-S" means the fluid-to-solid phase transition, N_0 and N_2 are given by (4.3.4), and $s_1^2 = s^2(1^+) = g_0(1^+) - 1$. It should be noticed that ${}^*\eta_+^{\text{pot}}(0)$ in (4.3.19A) is not the Newtonian viscosity coefficient, as mentioned before. But in the range of shear rate $|\Delta w_1| \ll (\tau\gamma) \ll 1$ it looks like the Newtonian viscosity coefficient, as can be seen in (4.3.19A). In the next paragraph b) the viscosity coefficients for the small region $(\tau\gamma) \ll \Delta w_1 \ll 1$ will be discussed,

where the Newtonian viscosity is very large in proportion to $(\Delta w_1)^{-1}$.

As one can see in the restriction of the range of shear rate, the asymptotic features (4.3.19A and B) are by no means of long range. It is not intended here that the asymptotic features (4.3.19A and B) are also valid in any range of larger shear rate, as some experiments show it /EVA,EHH/. The prediction of the nonanalytic behavior of the shear viscosity given by (4.3.19A) is essentially different from that of K. Kawasaki /KAW/ especially in describing the valid range of shear rate. To see the correct behaviors of the viscosity coefficients near the fluid-to-solid-like phase transition for the larger shear rates, $|\tau\gamma| \gg \Delta w_1 \ll 1$, one should return to the expression (4.3.18) which is rational function of the shear rate. To this end it is needed to have the correct functional form of equilibrium pair-correlation function for the system of molecules with the intermolecular potential (3.1.1). The asymptotic behaviors (4.3.19A and B) with their shear-rate range of validity are of physical importance in that they show the nonanalytic behavior, which implies the failure of the traditional perturbation expansion of the deviation $(g-g_0)$ with respect to the "total" shear rate at the phase transition (see 3.4)(v)).

Since one has the W-T solution for the $P-Y^{HS}$ equation, which is given by (3.2.14), the explicit form of (4.3.18) may be obtained for HS as follows:

$$H^s \eta_{\pm}^{pot}(\gamma) \cong \frac{48}{5\pi} (\tau_* \tau x^2 / \sigma^3) \sqrt{q_0(i^+)} \operatorname{Re} \left[\begin{matrix} \{1\} \\ -i \end{matrix} \right] \cdot \left[\frac{-(6+3S_1^2)(1-ik-k^2/3) + N(k)}{2k^2(1-ik)} \right],$$

where the expression (4.3.3) is introduced and the relation $x=\pi/6$ has been used. The rational function $N(k)$ given by (3.3.29D) may be rearranged in the following way

$$N(k) = (3 - i3k - k^2) s_1^> - k^2(1 - ik) \sum_{\ell}^{\#} \frac{u_{\ell}}{v_{\ell} + ik} - ik^3 \sum_{\ell}^{\#} \frac{u_{\ell}}{(v_{\ell} + ik)^2}, \quad (4.3.20)$$

where $s_1^> := s^>(1^+) = \varepsilon_1 u_1$.

On substituting (4.3.20) into the above expression one has for each component of viscosity coefficients

$${}^{HS}\eta_+^{\text{pot}}(\gamma) \cong E \operatorname{Re} \left[\frac{1}{1 - ik} - \frac{1}{2} \sum_{\ell}^{\#} \frac{u_{\ell}}{v_{\ell} + ik} - \frac{ik/2}{1 - ik} \sum_{\ell}^{\#} \frac{u_{\ell}}{(v_{\ell} + ik)^2} \right] \quad (4.3.21A)$$

and

$${}^{HS}\eta_-^{\text{pot}}(\gamma) \cong E \operatorname{Re} \left[i3k^{-2} - \frac{i}{1 - ik} + \frac{i}{2} \sum_{\ell}^{\#} \frac{u_{\ell}}{v_{\ell} + ik} - \frac{k/2}{1 - ik} \sum_{\ell}^{\#} \frac{u_{\ell}}{(v_{\ell} + ik)^2} \right], \quad (4.3.21B)$$

$$\text{where } E := (9.6/\pi) (T_* x^2 \tau / \sigma^3) g_0^{1/2} (1^+). \quad (4.3.21C)$$

Now one introduces for the state number # the fourth-order approximation (3.2.31) of density correlation function $s_{\text{PYH}}^>(r)$, and obtains the following numerical transition values of v_1 , v_2 , u_1 , u_2 by using the transition density x^* given by (4.3.13):

$$\begin{aligned} v_1^* &= \overline{v_2^*} = -(1.56\cdots) - i(4.41\cdots) \\ u_1^* &= \overline{u_2^*} = (3.10\cdots) - i(6.14\cdots) \end{aligned} \quad \text{for } x = x^*. \quad (4.3.22)$$

If one substitutes these values in (4.3.21A) and calculates for $|k| \ll 1$, one finds that the value of shear viscosity is almost zero. When the shear rate increases a little further, the shear viscosity coefficient shows the instability, i.e. has the

negative value. The values of shear rate at which the instability occurs are listed for the HS fluid with their corresponding densities in Table 4.3.1, where the W-T solution for the $P-Y^{HS}$ equation is used. As one can see in Table 4.3.1, the nearer the density approaches to the transition value x^* , the smaller the starting value of shear rate for instability becomes

It is perhaps possible that the negative value of the shear viscosity calculated here is caused by some approximations, which here is not further examined.

density: X	$\Delta w_1 = 3 - w_1$	Half-width of the peak of $\eta_+^{\text{pot}}(\sigma)$ $\sim (3 \Delta w_1)$	Height of the peak: $\eta_+^{\text{pot}}(\sigma)$ in the unit ($T_* \tau / \sigma^3$)	Maximum of $\eta_+^{\text{pot}}(\sigma)$		Values of the shear rate (σ) at the beginning of instability
				positions (σ)	values in the unit ($T_* \tau / \sigma^3$)	
0.5	0.3	0.9	$0.1139 \cdot 10^2$	0.810	0.595 10	2.776
0.52	0.0595	0.2	$0.6492 \cdot 10^2$	0.174	0.328 10^2	1.145
0.524	$0.8889 \cdot 10^{-2}$	$0.3 \cdot 10^{-1}$	$0.4455 \cdot 10^3$	$0.262 \cdot 10^{-1}$	$0.223 \cdot 10^3$	0.471
0.5246	$0.1217 \cdot 10^{-2}$	$0.4 \cdot 10^{-2}$	$0.3265 \cdot 10^4$	$0.36 \cdot 10^{-2}$	$0.163 \cdot 10^4$	0.198
0.52469	$0.6503 \cdot 10^{-4}$	$0.2 \cdot 10^{-3}$	$0.61160 \cdot 10^5$	$0.20 \cdot 10^{-3}$	$0.306 \cdot 10^5$	0.058
0.524695	$0.98 \cdot 10^{-6}$	$0.3 \cdot 10^{-5}$	$0.4054 \cdot 10^7$	$0.30 \cdot 10^{-5}$	$0.203 \cdot 10^7$	0.010

Table 4.3.1

The values of the viscosity coefficients near the fluid-to-solid-like phase transition for hard spheres, where the W-I solution for the P-Y^{HS} equation is used and the transition density is given by $X^* = \sqrt{1.05} - 0.5 = 0.524695 \dots$

b) $|k| < \Delta w_1 \ll 1$: A superhigh peak of the shear viscosity

This condition may be re-expressed by using (4.3.16,11):

$$(\tau\gamma)^{1/2} < \Delta w_1 = \{3 + 2^{-1}g_0'(1^+)/g_0(1^+)\} \ll 1. \quad (4.3.23)$$

Under this condition one cannot neglect the terms with Δw_1 in (4.3.17). The limiting functional forms of the viscosity coefficients in power series in k are the same as those calculated in the subsection (i) of 4.2) and given by (4.2.5A and B). For the HS system these may be written as follows:

$$HS_{\eta_+}^{pot}(\gamma) \approx HS_{\eta_+}^{pot}(0) \{1 - A_2^{HS}(\tau\gamma)^2\} \quad (4.3.24A)$$

$$HS_{\eta_-}^{pot}(\gamma) \approx (\tau\gamma) \cdot HS_{\eta_+}^{pot}(0) A_2^{HS}, \quad (4.3.24B)$$

where the Newtonian viscosity for hard spheres is given by

$$HS_{\eta_+}^{pot}(0) = (2\pi/15) (T_* \tau n^2 / \sigma^3) g_0^{1/2}(1^+) \{-b_0(1) - 2B_0\} \text{ from (4.2.6)}$$

$$= (4\pi/15) (T_* \tau n^2 / \sigma^3) g_0^{1/2}(1^+) / (3-w_1) \text{ from (App.1.7-8)}$$

$$\text{and (3.4.8-9),} \quad (4.3.24C)$$

and

$$A_2^{HS} = \{(2\pi/15) (T_* \tau n^2 / \sigma^3) / HS_{\eta_+}^{pot}(0)\} \{g_0^{1/2}(1^+) (-b_4(1) - 2B_0B_4)\}$$

from (4.2.7A)

$$= (7/288) (3-w_1)^{-2} + O(1/\Delta w_1) \text{ from (App.1.7-8), (3.4.8-9).}$$

$$(4.2.24D)$$

Near the transition the shear viscosity has a very high and narrow peak at $(\tau\gamma) = 0$, which becomes infinitely higher and infinitesimally narrower as the fluid system approaches to the

fluid-to-solid transition, until it disappears at the transition. The height of this peak is the value of Newtonian viscosity coefficient which is proportional to $(\Delta w_1)^{-1} = (3-w_1)^{-1}$, as can be seen in (4.3.24C) for HS. The width of this superhigh peak may be deduced from (4.3.17) and (4.3.13):

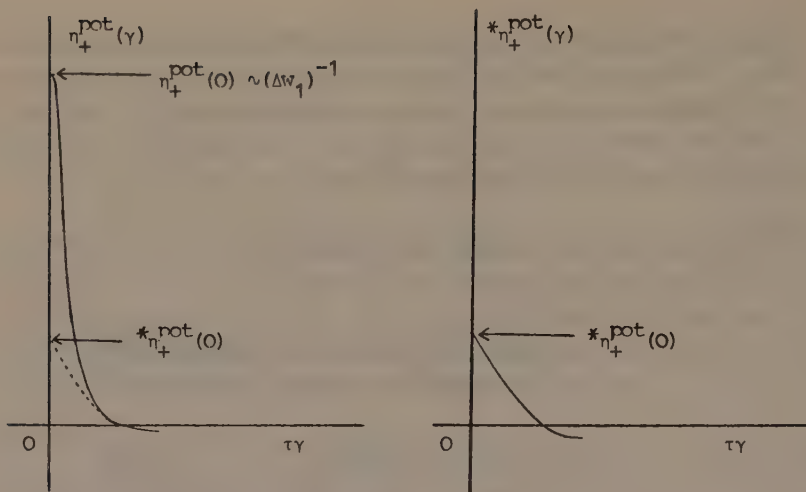
$$\begin{aligned} \eta_+^{\text{HS pot}}(\gamma) &\sim \text{Re} \left[-b(k, 1) - q(k, 1) \right] \\ &= \text{Re} \left[\frac{6(2+s_1^2)(1-ik-k^2/3) - q(k, 1)N(k)}{6\Delta w_1(1-ik) - 2\Delta w_1 k^2 - 2(1-ik)k^2} \right] \\ &\sim \text{Re} \left[\frac{6(2+s_1^2) - 2(3s_1^2)}{6\Delta w_1 - 2k^2} \right] = \frac{18\Delta w_1}{(3\Delta w_1)^2 + (\gamma\gamma)^2}, \end{aligned}$$

where the higher-order terms in $|k|$ ($<\Delta w_1$) are neglected and $N(k)$ is given by (4.3.4). As one can see in the above expression, the half-width of the peak is given by

$$(\text{half-width of the peak}) \sim (3\Delta w_1). \quad (4.3.25)$$

Thus the superhigh peak lies in the narrow range $0 < (\gamma\gamma) < (6\Delta w_1)$. The configuration of superhigh peak of shear viscosity coefficient just near the fluid-to-solid-like transition is shown in Fig.4.3.1. As discussed in the subsection (i) of 4.2), the ultimate limiting functional form of shear viscosity at $\gamma = 0$ is a concave parabola.

The viscosity coefficient of normal pressure difference increases abruptly from its zero value at $\gamma=0$ to its maximum, since the gradient $\{\eta_+^{\text{HS pot}}(0)A_2^{\text{HS}}\} \sim (\Delta w_1)^{-3}$ is a very large number for $(\Delta w_1) \ll 1$ in the left-hand side of the maximum, as can be seen in (4.3.24B-D). But one sees in (4.3.19B) that $\eta_-^{\text{pot}}(\gamma)$ decreases in the next region of $(\gamma\gamma)$ defined by the last paragraph a) in this subsection. Thus the viscosity coefficient of normal pressure difference has a very large positive



a) $0 < \Delta w_1 < 1$: near transition b) $\Delta w_1 = 0$: at transition

Fig.4.3.1: The superhigh peak of shear viscosity coefficient just near the fluid-to-solid-like phase transition:

a) The superhigh peak becomes higher and higher in proportion to $(\Delta w_1)^{-1}$ and its half-width ($3\Delta w_1$) becomes narrower and narrower, as $\Delta w_1 \rightarrow 0$, i.e. the fluid system approaches to the fluid-to-solid-like phase transition.

b) The superhigh peak now is squeezed and has disappeared. The shear viscosity coefficient has its finite limiting value $*\eta_+^{\text{pot}}(0)$ at $\gamma=0$.

value just near the η_-^{pot} -axis in its right-hand side. The distance between the maximum and the η_-^{pot} -axis may be deduced also from (4.3.17) and (4.1.13), and the position of maximum is always within the range $(\tau\gamma) < (6\Delta w_1)$, as can be seen in Table 4.3.1. At the transition, i.e. $\Delta w_1 = 0$ $\eta_-^{\text{pot}}(\gamma)$ goes to the infinity as $(\tau\gamma) \rightarrow 0$, and the normal pressure difference has its finite switching-on value $*P_-^{\text{pot}}(0^+)$ described in the last subsection.

Remark

Just near the fluid-to-solid-like phase transition, for which its condition is given by (4.3.11), the viscosity coefficients behave abnormally. At switching on the shear strain the shear viscosity has a very large value in proportion to $(\Delta w_1)^{-1}$ and decreases very abruptly for small increment of shear rate. For a further small increment of shear rate the shear viscosity has negative values. It is also possible that this negative values of the shear viscosity stems from the approximations which have been introduced. The superhigh peaks at $\tau\gamma=0$ and the instabilities of HS are shown for various densities near the transition in Table 4.3.1.

The normal pressure difference at the transition jumps from its zero value in equilibrium to the switching-on value $*P_{-}^{\text{pot}}(0^+)$ as soon as the shear strain is "switched on". This phenomenon occurs at the condition $\Delta w_1 := 3 - w_1 = 0$, which is given by (4.3.11) more explicitly, and here is interpreted as a fluid-to-solid-like phase transition of the molecular system.

The mean force which a molecule sees at the hard core in the relative pair space is given in equilibrium by

$$-2T_*w_1 := -w'(1^+) = T_*g'_0(1^+)/g_0(1^+).$$

The hard-sphere pair-correlation function has a negative gradient at the hard core almost over the whole range of density permitted, which can be seen in the W-T solution for the P-Y^{HS} equation. Thus it is expected that the equilibrium pair-correlation of the fluid system of molecules with the intermolecular potential (3.1.1) has a negative gradient at the hard core. This implies an attractive mean force at the hard core in the relative pair space. This attractive mean force near the hard core causes the packing effect of the neighbor molecules.

When the attractive mean force near the hard core has reached some critical value,

packing effect of neighbor molecules becomes so strong that the fluid-to-solid-like phase transition may occur.

The expression for $\eta_+^{\text{EHS pot}}(\gamma)$ stated above (4.3.25) may be written more correctly from (4.1.13) and (4.3.17) as follows

$$\begin{aligned} \eta_+^{\text{EHS pot}}(\gamma) &= \frac{2\pi}{15} (\tau_* \tau n^2 / \sigma^3) \sqrt{g_0(1+)} \cdot \\ &\quad \cdot \text{Re} \left[\frac{6(2+S_1^2)(1-ik-k^2/3) - 2N(k)}{6\Delta w_1(1-ik) - 2\Delta w_1 k^2 - 2(1-ik)k^2} \right] \\ &\sim \frac{2\pi}{15} (\tau_* \tau n^2 / \sigma^3) \sqrt{g_0(1+)} \cdot \left[\frac{6(2+S_1^2) - 2(3S_1^2)}{6\Delta w_1 - 2k^2} \right] \text{ for } |k| < \Delta w_1 \ll 1 \\ &= \frac{12\pi}{15} (\tau_* \tau n^2 / \sigma^3) \sqrt{g_0(1+)} \cdot \frac{(\tau / \Delta w_1)}{9 + (\gamma \tau / \Delta w_1)^2}, \end{aligned}$$

where $N(k)$ is given by (4.3.4) and the higher-order terms of k are neglected under the condition $|k| < \Delta w_1 \ll 1$.

The relaxation time τ , introduced in (2.2.2) formally now is associated with the factor $1/\Delta w_1$ which is very large just near the fluid-to-solid-like phase transition. Thus the superhigh peak effect of the shear viscosity just near the fluid-to-solid-like phase transition may be interpreted as the large value of the true relaxation time $(\tau/\Delta w_1)^{++}$. When the true relaxation time is so large, the molecules hardly forget something done on them and the fluid system behaves like a solid. But this occurs only for the small shear-rate range restricted to the condition $|k| < \Delta w_1 \ll 1$ just near the fluid-to-solid-like phase transition.

++The author is indebted to Professor S. Hess for pointing this out to him.

4.4) Graphs and remarks on the viscosity coefficients of hard spheres

In order to show the viscosity coefficients of hard spheres in graphs the expression (4.1.13) is transformed as follows:

$$\text{EHS } \eta_{\pm}^{\text{pot}}(\gamma) = \text{EHS } \eta_{+}^{\text{pot}}(0) \text{Re} \left[\left\{ \begin{array}{c} 1 \\ -i \end{array} \right\} \cdot \right. \\ \left. \frac{(1-ik - \frac{k^2}{3}) + \frac{k^2}{6}(1-ik) \sum_{\ell}^{\#} \frac{u_{\ell}}{v_{\ell}+ik} + \frac{ik^3}{6} \sum_{\ell}^{\#} \frac{u_{\ell}}{(v_{\ell}+ik)^2}}{1 - ik + Q_2 k^2 + iQ_3 k^3} \right] \quad (4.4.1)$$

where

$$\text{EHS } \eta_{+}^{\text{pot}}(0) = \frac{288}{5\pi} (\tau_* \tau / \sigma^3) (x^2 / Q_0) g_0^{1/2}(1+) \quad (4.4.1A)$$

is the Newtonian viscosity of hard spheres, Q_0 , Q_2 , and Q_3 are defined in (3.3.29D), and $k := \exp(i\pi/4) (\tau\gamma)^{1/2}$.

The statement number "#" is here replaced by (3.2.31), which implies that the values of the v_1 's and the u_1 's are given by those indicated in (3.2.31). It is here noted that the density correlation function given by (3.2.31) was obtained by using the W-T solution of the P-Y^{HS} equation.

The relaxation time τ was formally introduced by (2.2.2) and is related to the friction constant ζ . Since in this work one has no way to calculate the friction constant, the formally introduced relaxation-time τ is considered as a phenomenological parameter. For this reason the viscosity coefficients are scaled by $(\tau T_* / \sigma^3)$ and are shown graphically. The focus of attention is here to display the essential behavior of viscosity coefficients just near the fluid-to-solid-like phase transition

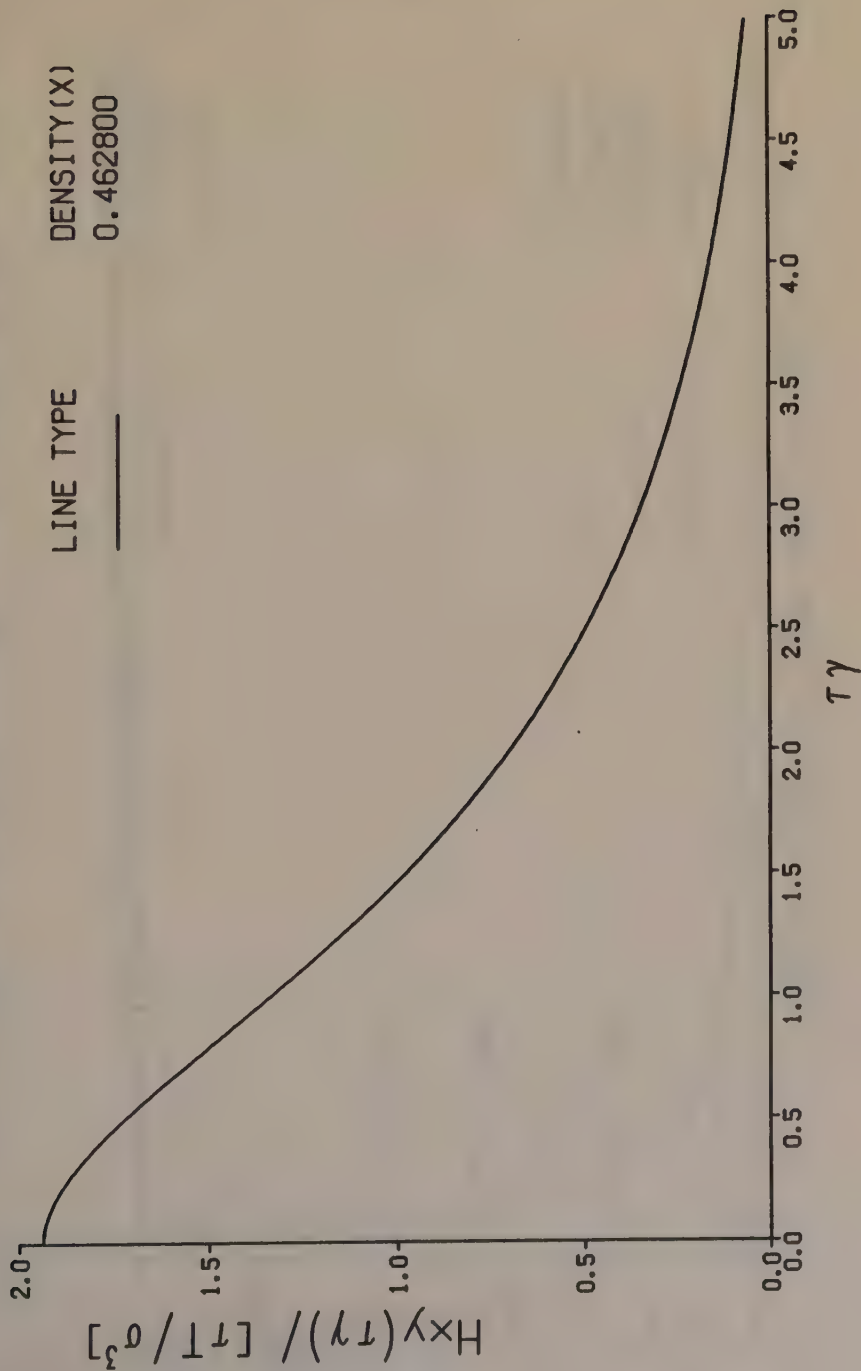
rather than to show their absolute values.

In Fig.4.4.1 one sees the curves of shear viscosity a little away from the fluid-to-solid-like phase transition. Its qualitative feature is similar to that of other theories and computer experiments/EYR,EU,HES3,EVA,A-H/.

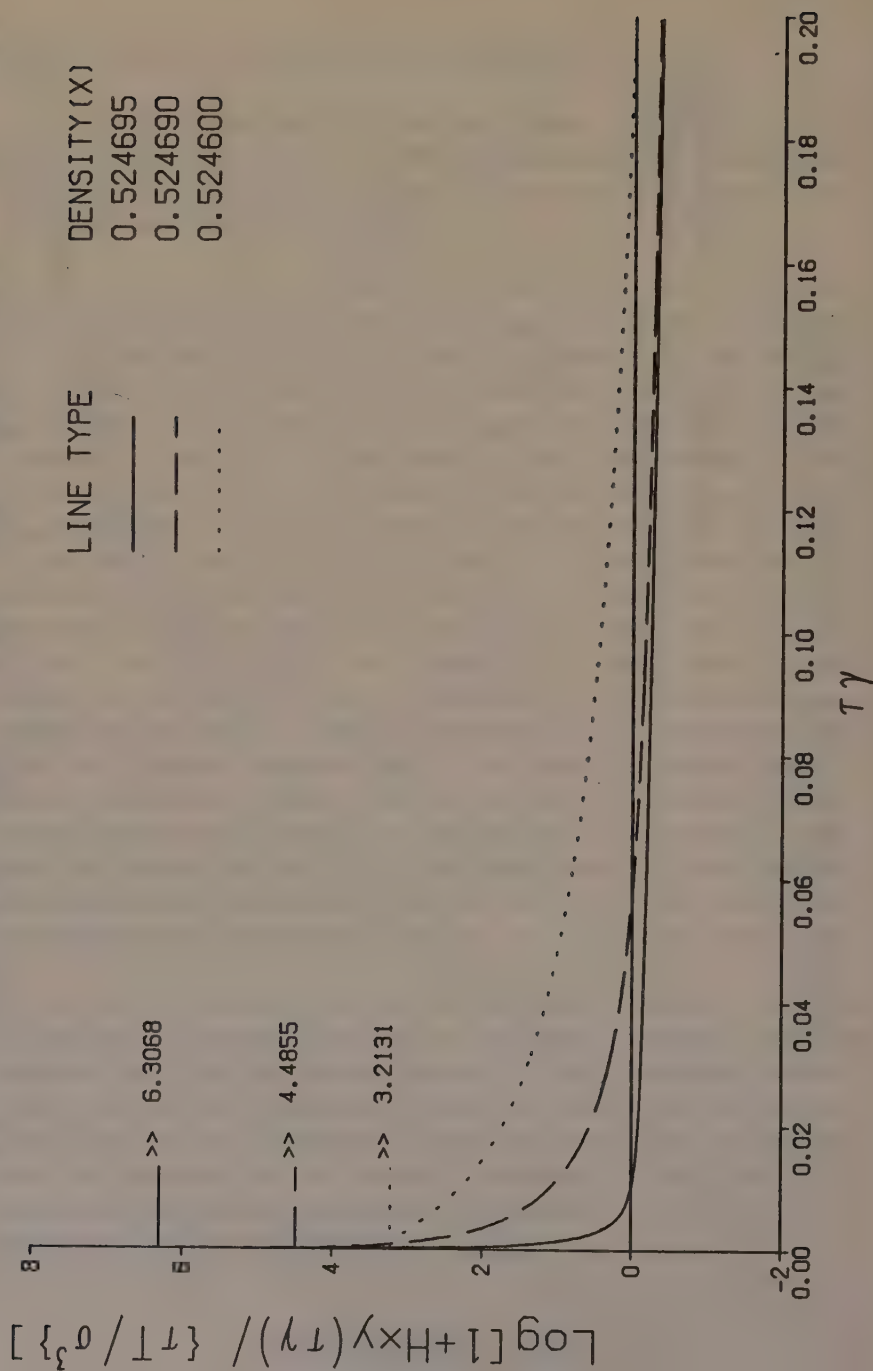
In Fig.4.4.2 the superhigh peak effect of shear viscosity just near the fluid-to-solid-like phase transition is displayed. As the density of hard spheres approaches to the transition density $x^* = (1.05)^{1/2} - 0.5 = 0.524695\dots$, the value of the Newtonian viscosity (the height of peak) becomes larger in proportion to $1/\Delta w_1$ and the half-width of the peak becomes smaller in proportion to Δw_1 . In order to see the full effect of the superhigh peak the relative deviation of density from the transition density should be within 0.001 %. As the shear rate increases, the (potential contribution to) shear viscosity coefficient is plunged into its minus values. This was explained in the last section as the instability of the fluid system. But it is not sure whether it is caused by the approximations introduced or not, as already mentioned. It is also possible that the kinetic contribution to the shear viscosity coefficient compensates for the negative value of the potential contribution and there occurs no instability in the fluid system. One can observe in Fig.4.4.2 that the value of shear rate at the beginning of instability becomes smaller as the density approaches to its transition value.

In Fig.4.4.3 the viscosity coefficient of normal pressure difference is depicted at the two different densities of hard spheres near the transition density. This viscosity coefficient reacts also very sensitively to the change of density near the fluid-to-solid-like phase transition, and its maximum goes to infinity, as the density approaches to the transition density. But the normal pressure difference remains finite, as mentioned in the last section.

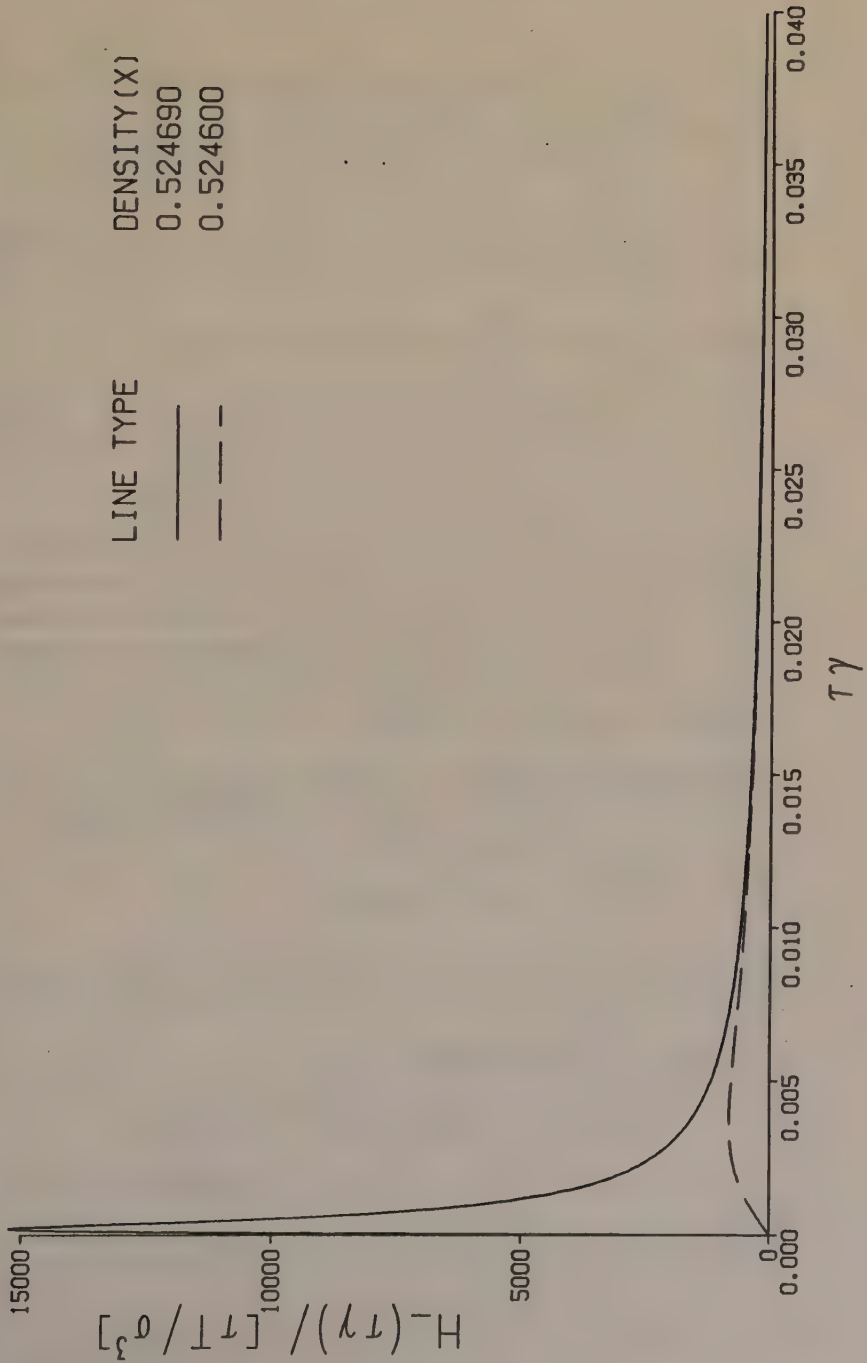
SHEAR VISCOSITY FOR HARD SPHERES



SHEAR VISCOSITY FOR HARD SPHERES



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App. 1) Expansion of $p(k,r)$, $b(k,r)$, $q(k,r)$, and $1/C_+^{(1)}$ in power series in k to the fourth order

The first term of the function $\hat{F}(k,r) = i p(k,r) + i b(k,r) + i q(k,r) B(k)$ defined by (3.4.5) may be written as

$$i p(k,r) = -i 2 k j_2(k r) \int_0^r n_2(k t) t^3 \left\{ \frac{1}{2} \tilde{s}(t) \right\}' dt + \\ + i 2 k n_2(k r) \int_0^r j_2(k t) t^3 \left\{ \frac{1}{2} \tilde{s}(t) \right\}' dt \quad (\text{app. 1.1})$$

from (3.3.21B, C), and (3.3.27).

Since the contribution of large r to the integral for the viscosity coefficients is negligible, as mentioned before, the upper limit of integrals, r may be considered to be small (at least not so large) and the Bessel functions above (both outside and inside the integrals) may be expanded in power series in k . Here the terms contributing to the fourth-order approximation of $i p(k,r)$ are taken.

For the frequent use one writes down the power expansions of spherical Bessel functions, $j_2(k r)$ and $n_2(k r)$, to the third term [ABR]:

$$j_2(k r) = \frac{(k r)^2}{15} \left\{ 1 - \frac{1}{14} (k r)^2 + \frac{1}{504} (k r)^4 - \dots \right\} \\ n_2(k r) = -3 (k r)^{-3} \left\{ 1 + \frac{1}{6} (k r)^2 + \frac{1}{24} (k r)^4 + \dots \right\}. \quad (\text{app. 1.2})$$

On defining the following integral

$$I^{(n)}(r) \equiv \int_0^r t^n \left\{ \frac{1}{2} \tilde{s}(t) \right\}' dt \quad \text{for } n \text{ integer}, \quad (\text{app. 1.3})$$

one has

$$\overset{r}{J}_A(k) \equiv \int_{1+}^F j_2(k, t) t^3 \left\{ \frac{1}{2} s(t) \right\}' dt$$

$$\approx \frac{1}{15} k^2 \left\{ I^{(5)}(r) - \frac{1}{14} k^2 I^{(7)}(r) + \frac{1}{504} k^4 I^{(9)}(r) \right\}$$

$$\overset{r}{N}_A(k) \equiv \int_{1+}^F n_2(k, t) t^3 \left\{ \frac{1}{2} s(t) \right\}' dt$$

$$\approx -3 k^{-3} \left\{ I^{(0)}(r) + \frac{1}{6} k^2 I^{(2)}(r) + \frac{1}{24} k^4 I^{(4)}(r) \right\} \quad (\text{app. 1.4})$$

Substitution of (app. 1.2, 4) into (app. 1.1) leads to:

$$i p(k, r) \approx i p_0(r) + i p_2(r) k^2 + i p_4(r) k^4$$

with

$$p_0(r) \equiv \frac{2}{5} r^2 I^{(0)}(r) - \frac{2}{5} r^{-3} I^{(5)}(r)$$

$$p_2(r) = -\frac{r^4}{35} I^{(0)}(r) + \frac{r^2}{15} I^{(2)}(r) - \frac{r^{-1}}{15} I^{(5)}(r) + \frac{r^{-3}}{35} I^{(7)}(r)$$

$$p_4(r) \equiv \frac{1}{1260} \left\{ r^6 I^{(0)}(r) - 6 r^4 I^{(2)}(r) + 21 r^2 I^{(4)}(r) - \right. \\ \left. - 21 r I^{(5)}(r) + 6 r^{-1} I^{(7)}(r) - r^{-3} I^{(9)}(r) \right\} \quad , \\ (\text{app. 1.5})$$

where it is noted that $p_0(r)$, $p_2(r)$, and $p_4(r)$ are real functions. In (app. 1.5) the linear and the third-order term in k don't appear.

The second term of $\overset{0}{F}(k, r)$, $i b(k, r)$, may be expanded more exactly in its $j_2(k, r) - n_2(k, r)$ -representation:

$$i b(k, r) = i(1 + \delta_{1,r}) \sqrt{g_{\delta}(1^+)} h_2^{(1)}(k, r) / C_+^{(1)}$$

$$= i(1 + \delta_{1,r}) \sqrt{g_{\delta}(1^+)} \left\{ j_2(k, r) + i n_2(k, r) \right\} / \left\{ \frac{1}{2} T_*^{-1} \omega'(1^+) j_2(k) + \right. \\ \left. + \left(\frac{\partial}{\partial t} j_2(k, t) \right)_{t=1} + i \frac{1}{2} T_*^{-1} \omega'(1^+) n_2(k) + i \left(\frac{\partial}{\partial t} n_2(k, t) \right)_{t=1} \right\} \quad .$$

Since $j_2(kr) \sim (kr)^2$ and $n_2(kr) \sim (kr)^{-3}$, one may neglect in the above expression the spherical Bessel function of first kind $j_2(kr)$ in the fourth-order approximation in k . One obtains for $1/C_+^{(1)}$:

$$1/C_+^{(1)} \approx \left\{ i \omega_1 n_2(k) + i \left(\frac{\partial}{\partial t} n_2(k, t) \right)_{t=1} \right\}^{-1}, \quad (\text{app. 1.6})$$

where $\omega_1 \equiv \frac{1}{2} T_*^{-1} w'(1^+)$.

Making use of the expansion (app. 1.2) leads to

$$1/C_+^{(1)} \approx \frac{1}{3i} k^3 C_0^{(1)} \left\{ 1 + C_2^{(1)} k^2 + C_4^{(1)} k^4 \right\}$$

with $C_0^{(1)} \equiv 1/(3 - \omega_1)$

$$C_2^{(1)} \equiv \frac{1}{6} (\omega_1 - 1)/(3 - \omega_1)$$

$$C_4^{(1)} \equiv \frac{1}{72} (11 + 2\omega_1 - \omega_1^2)/(3 - \omega_1)^2, \quad (\text{app. 1.7})$$

where $C_0^{(1)}$, $C_2^{(1)}$, and $C_4^{(1)}$ are real, and the linear and the third-order term in k don't appear. In the above calculation the following condition is tacitly assumed:

$$\omega_1 \neq 3. \quad (\text{app. 1.7A})$$

This condition is related to the fluid-solid phase transition discussed in 4.3).

The result (app. 1.7) may be substituted into the above expression for $i b(k, r)$, and using the expansion (app. 1.2) one obtains

$$\begin{aligned} i b(k, r) &\approx i(1 + \delta_{1,r})(1 + \tilde{s}_1/2) n_2(kr) \frac{k^3}{3} C_0^{(1)} \left\{ 1 + C_2^{(1)} k^2 + C_4^{(1)} k^4 \right\} \\ &\approx i b_0(r) + i b_2(r) k^2 + i b_4(r) k^4 \end{aligned}$$

with

$$b_0(r) \equiv -(1 + \delta_{4,r})(1 + s_1^2/2) C_0^{(1)} \cdot r^{-3}$$

$$b_2(r) \equiv b_0(r) \left\{ r^2/6 + C_2^{(1)} \right\}$$

$$b_4(r) \equiv b_0(r) \left\{ r^4/24 + (r^2/6) C_2^{(1)} + C_4^{(1)} \right\} \quad , \quad (\text{app. 1.8})$$

where $b_0(r)$, $b_2(r)$, and $b_4(r)$ are real functions, and the linear and the third-order term in k don't appear.

The first factor of the third term of $F(k,r)$, $i q(k,r)$, may be easily expanded in power series of k , and one has its fourth-order approximation, making use of (app. 1.2), as follows

$$i q(k,r) = -2 i k \left\{ \omega_1 j_2(k) + \left(\frac{\partial}{\partial t} j_2(k t) \right)_{t=1} \right\} n_2(k r) +$$

$$+ 2 i k \left\{ \omega_1 n_2(k) + \left(\frac{\partial}{\partial t} n_2(k t) \right)_{t=1} \right\} j_2(k r) \quad \begin{array}{l} \text{from (3.4.5)} \\ \text{and (3.3.25B)} \end{array}$$

$$\approx i q_0(r) + i q_2(r) k^2 + i q_4(r) k^4$$

with

$$q_0(r) \equiv \frac{2}{5} (2 r^{-3} + 3 r^2) + \frac{2}{5} \omega_1 (r^{-3} - r^2)$$

$$q_2(r) \equiv \frac{1}{105} (-12 r^{-3} + 14 r^{-1} + 7 r^2 - 9 r^4) +$$

$$+ \frac{\omega_1}{105} (-3 r^{-3} + 7 r^{-1} - 7 r^2 + 3 r^4)$$

$$q_4(r) \equiv \frac{1}{420} (2 r^{-3} - 8 r^{-1} + 14 r - 7 r^2 - 2 r^4 + r^6) +$$

$$+ \frac{\omega_1}{1260} (r^{-3} - 6 r^{-1} + 21 r - 21 r^2 + 6 r^4 - r^6)$$

and $\omega_1 \equiv \frac{1}{2} \tau_*^{-1} \omega'(1^+)$, (app. 1.9)

where $q_0(r)$, $q_2(r)$, and $q_4(r)$ are real functions, and the linear and the third-order term in k don't appear again.

Zusammenfassung

Die vielfältig varierende Abhängigkeit der Paarkorrelationsfunktion von der Scherrate wurde durch die Lösung der in dieser Arbeit erweiterten Kirkwood-Smoluchowski(K-S)-Gleichung für die Paarkorrelationsfunktion in der Couette-Strömung erhalten. Diese erweiterte K-S-Gleichung wurde aus Kirkwoods verallgemeinerter Fokker-Planck-Gleichung abgeleitet, wobei sowohl ihre Anwendungsmöglichkeit für große Strömungsgeschwindigkeiten als auch die Beschleunigung der Strömungsgeschwindigkeit berücksichtigt wurden. Bei der Lösung wurde der Deformationseffekt der Strömung als Störung betrachtet und ihr Rotationseffekt exakt berücksichtigt. Hier wurde nur die erste Näherung bezüglich des Deformationsparameters berechnet, aber die höheren Näherungen können durch dieselbe Greensche Funktion systematisch durchgeführt werden. Das Hauptinteresse war der Zusammenhang des Verhaltens der Paarkorrelationsfunktion sowie der daraus berechneten Viskositätskoeffizienten mit den Phasenübergängen (flüssig-fest und flüssig-gasförmig).

Das intermolekulare Potential wurde angesetzt als ein (effektiver) harte-Kugel-Anteil und ein weitgehend anziehender Anteil. Dieses intermolekulare Potential spielte bei allen Berechnungen eine fundamentale Rolle.

Die Ornstein-Zernike(O-Z)-Theorie der Dichte-Dichte-Korrelation im Gleichgewicht wurde eingeführt. Die Probleme bei ihrem Näherungsverfahren wurden diskutiert und ihre Näherung wurde verbessert. Diese verbesserte O-Z-Näherung war dafür notwendig, daß man die Lösung der K-S-Gleichung für die Paarkorrelationsfunktion im Nichtgleichgewicht sowie ihr mit dem flüssig-gasförmig-Phasenübergang verbundenes Verhalten explizit sehen kann.

Es wurde festgestellt, daß die Paarkorrelationsfunktion und die Viskositätskoeffizienten an der Stelle (oder in der Nähe) der beiden Phasenübergänge (flüssig-fest und flüssig-gasförmig)

nichtanalytisches Verhalten (für kleine Scherraten) zeigen. Bei diesem nichtanalytischen Verhalten ist wichtig, daß an der Stelle (oder in der Nähe) der beiden Phasenübergänge die traditionelle Störungsrechnung (bezüglich der "ganzen" Scherrate) nicht anwendbar ist.

Die Viskositätskoeffizienten verhalten sich exotisch an der Stelle (oder in der Nähe) des flüssig-fest-Phasenüberganges. An diesem Phasenübergang springt die Normaldruckdifferenz von ihrem Nullwert im Gleichgewicht auf einen endlichen Wert sobald die Scherströmung "eingeschaltet" ist. Eine enorm hohe und (dazu umgekehrt proportional) schmale Spitze ("superhigh peak") des Scherviskositätskoeffizienten zeigt sich an der Nullstelle der Scherrate ganz in der Nähe des flüssig-fest-Phasenüberganges. Da die Höhe dieser Spitze mit der Relaxationszeit verbunden ist, wird die wahre Relaxationszeit sehr groß ganz in der Nähe des flüssig-fest-Phasenüberganges und die Flüssigkeit verhält sich wie ein Festkörper. Eine Gleichung für diesen flüssig-fest-Phasenübergang wurde gefunden. Diese wurde durch die Wertheim-Thiele-Lösung der Percus-Yevick-Gleichung für harte Kugeln getestet. Die berechnete Übergangsdichte stimmt mit dem Experiment (Alder und Wainwright) gut überein.

Durch die Lösung dieser Gleichung kann man die Dichte-Temperatur-Beziehung für den flüssig-fest-Phasenübergang in den realistischen Flüssigkeiten darstellen, wobei die genaue Berechnung der effektiven Kraft im Gleichgewicht an der effektiven harten Kugel im relativen Zweiteilchenortsraum notwendig ist.

Die Berechnung des Reibungskoeffizienten ist erforderlich, um eine quantitative Abschätzung der Viskositätskoeffizienten zu erhalten.

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